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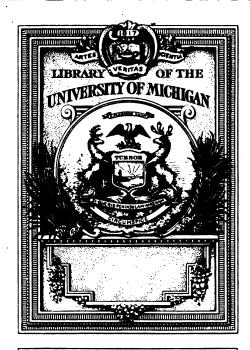
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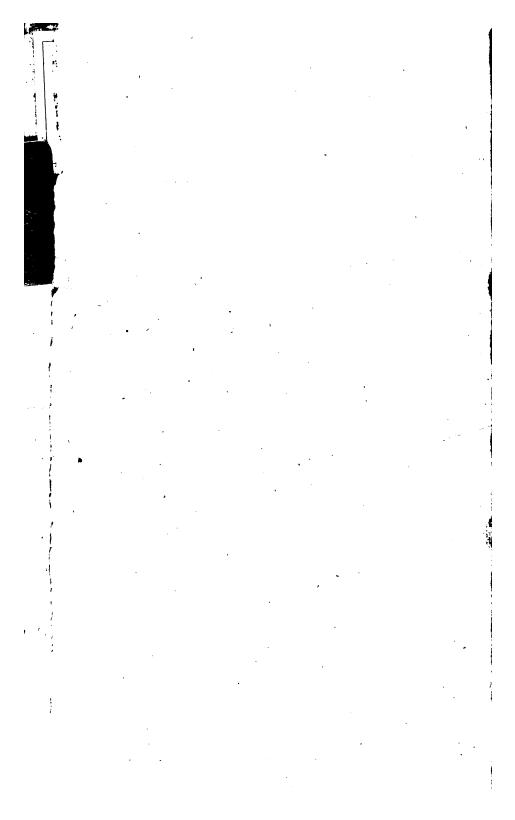
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ANN ARBOR, MICH.





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## **ELEMENTS**

OF

# EXPERIMENTAL CHEMISTRY,

BY

### WILLIAM HENRY, M.D.F.R.S.

Vice-Pres. of the Lit. and Phil. Soc. at Manchester; Mem. of the Rov. Med. and Wernerian Societies at Edinburgh; the Medice-Chirurgical and Geological Societies of London; the Physical Soc. of Jena; the Nat. Hist. Soc. of Moscow, &c. &c.

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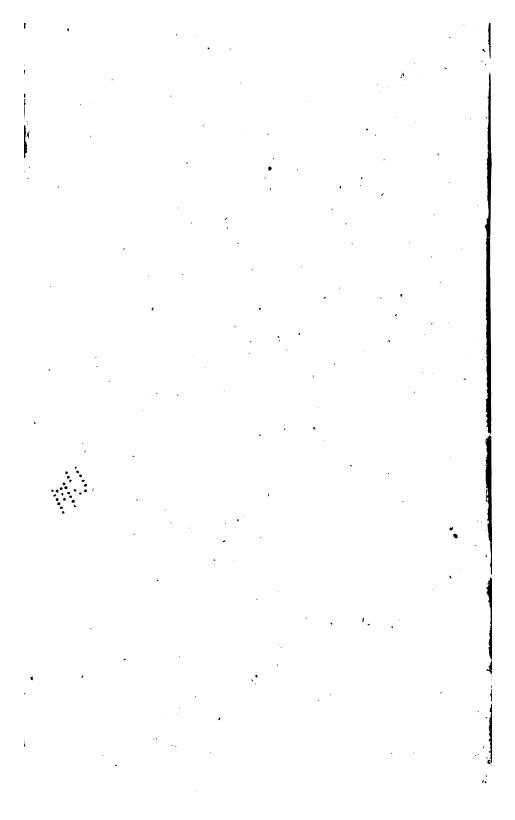
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1819.



### MR. JOHN DALTON,

President of the Lit. and Phil. Soc. of Manchester; Member of the Academy of Sciences of the Royal Institute of France; &c.

### A TESTIMONY OF RESPECT

FOR THE

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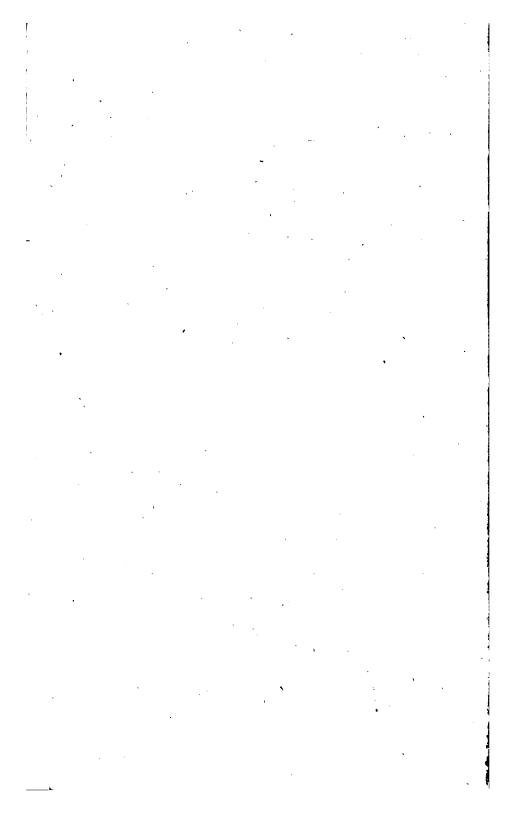
CHEMICAL PHILOSOPHY,

this work is inscribed.

BY HIS FRIEND,

THE AUTHOR.

Manchester, Oct. 1818.



Chem. til. From the Estate the Prof. E. B. Campbell 5-13-27

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TO THE

### EIGHTH LONDON EDITION.

During the interval which has elapsed since the publication of the last edition of this work, the progress of Chemistry, though not distinguished by essential changes in the general principles of the science has nevertheless been marked, not only by beneficial applications of those principles to the useful arts, but by the discovery of a great number of important facts, and of some new and interesting bodies. Among practical inventions, the Safety Lamp of Sir Humphry Davy stands pre-eminent, as a contribution from science to the interest of humanity, not resulting from accident, but suggested by general reasoning, and perfected by an admirable train of philosophical induction.-To our knowledge of individual bodies has been added that of a new alkali, a new earth, and two new metals; of a gas which, like chlorine, becomes acidified by union with hydrogen; of new acids, composed of oxygen in combination with chlorine, with nitrogen, and with phosphorus: and of compounds before undiscovered, derived from the vegetable and animal kingdoms. In a variety of instances, the properties of bodies, that had been long known, have been better ascertained and more extensively investigated. Such additional evidence, too, of the nature of chlorine has arisen out of the further controversy respecting it, as to have satisfied me of the propriety of a change in its classification. It has been necessary, therefore, again to revise the whole work with the greatest care; to make considerable additions to many of the sections; and to introduce a few entirely new ones. In a chapter of ADDENDA, also, at the close of the second volume, the history of discoveries will be found continued to the latest period which the publication would admit.

room for these improvements, without much enlarging the bulk of the volumes, I have rejected every thing which recent experience has corrected or rendered doubtful.

Though no pains have been spared to render the work a faithful abstract to the present state of Chemistry, yet it is not improbable that errors and omissions may still be discovered in it. In rectifying these, I hope to be assisted by a continuance of those candid criticisms, both through public and private channels of communication, to which I have already been greatly indebted.

Manchester, Oct. 1818.

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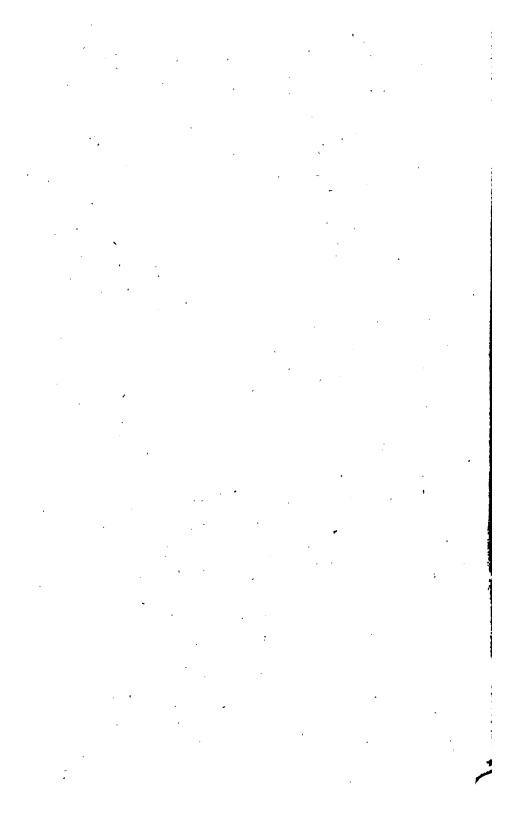
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## INTRODUCTION\*.

IT has so long been a custom to preface a course of lectures with the history of the science which is their object, that it may be necessary to state, briefly, the reasons that have induced me to depart from this established usage.

The history of chemistry may either be merely a history of the science, that is, a view of the progressive development of the facts and doctrines of which the science is composed; or it may comprehend, also, the biography of chemists. The detail of the progress of discovery, however, concerning particular objects of chemical research, would certainly be premature, at a period, when the student may be supposed to be ignorant of the external forms, and even of the existence, of no inconsiderable part of them. Respecting chemists themselves, little can be said that can contribute to information or amusement; for their lives, devoted to the abstract pursuits of science, have seldom been productive of events, that are suited to awaken or gratify general curiosity, Our interest, indeed, respecting philosophers, is seldom excited, unless by a knowledge of the additions which they have made to the facts or theories of a science; and with these a lecturer may fairly presume, however the fact may really be, that his heavers, at the commencement of a course, are wholly unacquainted. On these grounds, therefore, I hope to be excused for devoting to other purposes the time, that would have been allotted to the history of the science. For this, will be substituted a brief view of the nature and objects of chemistry; of its connexion with the arts and with other sciences; and an outline of the plan on which the following lectures will be conducted.

Vol. I—B

<sup>\*</sup> The following discourse formed, originally, the introduction to a series of lectures delivered in Manchester, and was afterwards published under the title of "A General View of the Nature and Objects of Chemistry, and of its Application to Arts and Manufactures." As the readers of an elementary book may be presumed to require a similar plan of instruction, with the hearers of a popular course of lectures, I have thought it unnecessary to alter the form under which the essay first appeared, though a few passages are applicable chiefly to the persons to whom it was originally addressed.

Natural philosophy, in its most extensive sense, is a term comprehending every science, that has for its objects the properties and affections of matter. But it has attained, by the sanction of common language, a more limited signification; and chemistry, though strictly a branch of natural philosophy, is generally regarded as a distinct science. Between the two it may, perhaps, be difficult to mark out precisely the line of separation: but, an obvious character of the facts of natural philosophy is, that they are always attended with sensible motion; and the determination of the laws of motion is peculiarly the office of its cultivators. Chemical changes, on the other hand, of the most important kind, often take place without any apparent motion, either of the mass, or of its minute parts; and where the eye is unable to perceive that any change has occurred. The laws of gravitation, of central forces, and all the other powers that fall under the cognizance of the natural philosopher, produce, at most, only a change of place in the bodies that obey their influence. But, in chemical changes, we may always observe an important difference in the properties of things: their appearances and qualities are completely altered, and their individuality destroyed. Thus, two highly corrosive substances, by uniting chemically together, may become mild and harmless; the combination of two colourless substances may present us with a compound of brilliant complexion; and the union of two fluids, with a compact and solid mass.

Chemistry, therefore, may be defined, that science, the object of which is to discover and explain the changes of composition that occur among the integrant and constituent parts of different bodies.\*

From this definition, it may readily be conceived, how wide is the range of chemical inquiry; and, by applying it to the various events that daily occur in the order of nature, we shall be enabled to separate them with accuracy; and to allot, to the sciences of natural philosophy and chemistry, the proper objects of the cultivation of each. Whenever a change of place is a necessary part of any event, we shall call in the aid of the former. When this condition may be dispensed with, we shall resort to chemistry for

<sup>\*</sup> The reader, who wishes to examine other definitions of chemistry, will find a variety of them, collected by Dr. Black, in the first volume of his "Lectures," published, since his death, by Professor Robison.

the light of its principles. But it will be often found, that the concurrence of the two sciences is essential to the full explanation of phenomena. The water of the ocean, for example, is raised into the atmosphere by its chemical combination with the matter of heat; but the clouds, that are thus formed, maintain their elevated situation by virtue of a specific gravity inferior to that of the lower regions of the air,—a law, the discovery and application of which are due to the natural philosopher, strictly so called.

It has not been unusual to consider chemistry, under the twofold view of a science and of an art. This arrangement, however, appears to have had its origin in an imperfect discrimination between two objects, that are essentially distinct. Science consists of assemblages of facts, associated together in classes, according to circumstances of resemblance or analogy. The business of its cultivators is, first, to investigate and establish individual truths, either by the careful observation of natural appearances, or of new and artificial combinations of phenomena produced by the instruments of experiment. The next step is the induction, from well ascertained facts, of general principles or laws, more or less comprehensive in their extent, and serving, like the classes and orders of natural history, the purposes of an artificial arrangement. Of such a body of facts and doctrines, the science of chemistry is composed. But the employment of the artist consists merely in producing a given effect, for the most part by the sole guidance of practice or experience. In the repetition of processes, he has only to follow an established rule; and, in the improvement of his art, he is benefited generally by fortuitous combinations, to which he has not been directed by any general axiom. An artist, indeed, of enlarged and enlightened mind, may avail himself of general principles, and may employ them as an useful instrument in perfecting established operations: but the art and the science are still marked by a distinct boundary. In such hands, they are auxiliaries to each other; the one contributing a valuable accession of facts; and the other, in return, imparting fixed and comprehensive principles, which simplify the processes of art, and direct to new and important practices.

The possession of the general principles of chemistry enables us to comprehend the mutual relation of a great variety of events, that form a part of the established course of nature. It unfolds the most sublime views of the beauty and harmony of the universe; and developes a plan of vast extent, and uninterrupted order, which could have been conceived only by perfect wisdom, and executed by unbounded power. By withdrawing the mind, also, from pursuits and amusements that excite the imagination, its investigations may tend, in common with the rest of the physical sciences, to the improvement of our intellectual and moral habits; to strengthen the faculty of patient and accurate thinking; and to substitute placid trains of feeling, for those which are too apt to be awakened by the contending interests of men in society, or the imperfect government of our own passions.

The class of natural events that call for the explanation of chemical science, is of very considerable extent; and the natural philosopher (using this term in its common acceptation) is wholly incompetent to unfold their connexion. He may explain, for example, on the principles of his own science, the annual and diurnal revolutions of the Earth, and part of the train of consequences depending on these rotations But here he must stop; and the chemist must trace the effects, on the Earth's surface, of the caloric and light derived from the sun; the absorption of caloric by the various bodies on which it falls; the consequent fluidity of some, and volatilization of others; the production of clouds, and their condensation in the form of rain; and the effects of this rain, as well as of the sun's heat, on the animal, vegetable, and mineral kingdoms. In these minuter changes, we shall find, there is not less excellence of contrivance, than in the stupendous movements of the planetary system. And they interest us even more nearly; because, though not more connected with our existence or comfort, yet they are more within our sphere of observation; and an acquaintance with their laws admits of a more direct application to human affairs.

There is another branch of knowledge (that of natural history), which is materially advanced by the application of chemical science. The classifications of the naturalist are derived from an examination and comparison of the external forms, both of animate and inanimate bodies. He distributes the whole range of nature into three great and comprehensive kingdoms,—the animal, the vegetable, and the mineral. Each of these, again, is subdivided into several less extensive classes; and individual ob-

jects are referred to their place in the system, by the agreement of their characters, with those assigned to the class, order, and genus. In the different departments of natural history, these resemblances vary in distinctness, in facility of observation, and in certainty of description. Thus, the number and disposition of the parts of fructification in vegetables afford marks of discrimination, which are well defined, and easily ascertained. But minerals, that are not possessed of a regularly crystallized form, are distinguished by outward qualities that scarcely admit of being accurately conveyed by language; such as minute shades of colour; or trifling differences of hardness, transparency, &c. the evidence of these loose and varying characters, that of the chemical composition of minerals has within the few past years been added; and mineralogy has been advanced, from a confused assemblage of its objects, to the dignity of a well methodized and scientific system. In the example of crystallized bodies, the correspondence between external form and chemical composition. has been most successfully traced by the genius of Hauy; whose method of investigation has enabled him, in numerous instances. to anticipate, from physical characters, the results of the most skilful and laborious analysis.

It is unnecessary to pursue this part of the subject to a greater extent; because, to all who have been in the habit of philosophical investigation, the connexion between the sciences must be sufficiently apparent; and because there is another ground, on which chemistry is more likely to claim, with success, the respect and attention of the great mass of mankind. This is, its capacity of ministering to our wants and our luxuries, and of instructing us to convert to the ordinary purposes of life, many substances which nature presents in a rude and useless form. The extraction of metals from their ores; the conversion of the rudest materials into the beautiful fabrics of glass and porcelain; the production of wine, ardent spirits, and vinegar; and the dyeing of linen, cotton, and woollen manufactures,—are only a few of the arts that are dependent on chemistry for their improvement, and even for their successful practice.

It cannot, however, be denied, that all the arts which have been mentioned were practised in times when the rank of chemistry, as a science, was extremely degraded; and that they are the daily employment of unlettered and ignorant men. But to what does

this confession amount? and how far does it prove the independence of the above arts on the science of chemistry?

The skill of an artist is compounded of knowledge and of manual dexterity. The latter, it is obvious, no science can teach.-But the acquirement of experience, in other words, a talent for the accurate observation of facts, and the habit of arranging facts in the best manner, may be greatly facilitated by the possession of scientific principles. Indeed, it is hardly possible for any one to frame rules for the practice of a chemical art, or to profit by the rules of others, who is unacquainted with the general doctrines of the science. For, in all rules, it is implied, that the promised effect will only take place, when circumstances are precisely the same as in the case under which the rule was formed. an unerring uniformity of result, the substances, employed in chemical process, must be of uniform composition and excellence; or, when it is not possible to obtain them thus unvaried, the artist should be able to judge precisely of the defect, that he may proportion his agents according to their qualities. Were chemical knowledge more generally possessed, we should hear less of failures and disappointments in chemical operations; and the artist would commence his proceedings, not, as at present, with distrust and uncertainty, but with a confident and well grounded expectation of success.

It will scarcely be contended, that any one of the arts has hitherto attained the extent of its possible perfection. In all, there is yet a wide scope for improvement, and an extensive range for ingenuity and invention. But from what class of men are we to expect useful discoveries? Are we to trust, as hitherto, to the favour of chance and accident: to the fortuitous success of those who are not guided in their experiments by any general principles? Or shall we not rather endeavour to inform the artist, and induce him to substitute, for vague and random conjecture, the torch of induction and of rational analogy? In the present imperfect state of his knowledge, the artist is even unable fully to avail himself of those fortunate accidents, by which improvements sometimes occur in his processes; because, to the eye of common observation, he may have acted agreeably to established rules, and have varied in circumstances which he can neither perceive nor appreciate. The man of science, in these instances, sees more

deeply, and, by availing himself of a minute and accidental difference, contributes at once to the promotion of his own interest, and to the advancement of his art.

But it is the union of theory with practice that is now recommended. And "when theoretical knowledge and practical skill are happily combined in the same person, the intellectual power of man appears in its full perfection, and equally fits him to conduct, with a masterly hand, the details of ordinary business, and to contend successfully with the untried difficulties of new and perplexing situations. In conducting the former, mere experience may frequently be a sufficient guide; but experience and speculation must be combined to prepare us for the latter\*." "Expert men," says Lord Bacon, "can execute and judge of particulars one by one; but the general counsels, and the plots, and the marshalling of affairs, come best from those that are learned."

This recommendation to artists, of the acquirement of scientific knowledge, is happily sanctioned by the illustrious success in our own days, of the application of theory to the practice of certain arts. Few persons are ignorant of the benefits that have resulted to the manufactures of this country, from the inventions of Mr. Watt and Mr. Wedgwood; both of whom have been not less benefactors of philosophy than eminent for practical skill. The former, by a clear insight into the doctrine of latent heat, resulting, in a great measure, from his own acuteness and patience of investigation, and seconded by an unusual share of mechanical skill, has perhaps brought the steam-engine to its acme of perfection. Mr. Wedgwood, aided by the possession of extensive chemical knowledge, made rapid advances in the improvement of the art of manufacturing porcelain; and, besides raising himself to great opulence and distinction, has created for his country a source of most profitable and extensive industry. In an art, also, which is nearly connected with the manufactures of our own town, and the improvement of which must, therefore, "come home to our business and bosoms, "we owe unspeakable obligations to two speculative chemists,-to Scheele, who first discovered the oxygenized muriatic acid; and to Berthollet, who first instructed us in its application to the art of bleaching.

<sup>\*</sup> Stewart's Elements of the Philosophy of the Human Mind, chap. iv. 'sect. 7.

Examples, however, may be urged against indulgence in theory: and instances are not wanting, in which the love of speculative refinement has withdrawn men entirely from the straight path of useful industry, and led them on gradually to the ruin of their fortunes. But from such instances, it would be unfair to deduce a general condemnation of theoretical knowledge. It would be the common error of arguing against things that are useful, from their occasional abuse.-In truth, projects which have, for their foundation, a dependence on chemical principles, may be undertaken with a more rational confidence, than such as have in view the accomplishment of mechanical purposes; because, in chemistry, we are better able, than in mechanics, to predict, from an experiment on a small scale, the probable issue of more extensive attempts. one, from the successful trial of a small machine, can affirm, with unerring certainty, that the same success will attend one on a greatly enlarged plan; because the amount of the resistances, that are opposed to motion, increases often into a ratio greater than, from theory, could ever have been foreseen: but the same law, by which the mineral alkali is extracted from a pound of common salt, must equally operate on a thousand times the quantity; and, even when we augment our quantities in this immense degree, the chemical affinities, by which so large a mass is decomposed, are exerted only between very small particles. The failures of the mechanic, therefore, arise from the nature of things; they occur, because he has not in his power the means of foreseeing and calculating the causes that produce them. But, if the chemist fail in perfecting an economical scheme on a large scale, it is either because he has not sufficiently ascertained his facts on a small one, or has rashly embarked in extensive speculations, without having previously ensured the accuracy of his estimates.

The benefits which we are entitled to expect from the efforts of the artist and the man of science, united in one peoson, and at the same time tempered and directed by prudential wisdom, affect not only individual but national prosperity. To the support of its distinction, as a commercial nation, this country is to look for the permanency of its riches, its power, and, perhaps, even of its liberties; and this pre-eminence is to be maintained, not only by local advantages, but on the more certain ground of superiority in the productions of its arts. Impressed with a full conviction

of this influence of the sciences, a neighbouring and rival people offer the most public and respectful incitements to the application of theory in the improvement of the chemical arts; and, with the view of promoting this object, national institutions have been formed among them, which have been already, in several instances, attended with the most encouraging success. It may be sufficient, at present, to mention, as an example, that France, during a long war, supplied, from her own native resources, her enormous, and perhaps, unequalled consumption of nitre.

The general uses of chemistry have been thus fully enlarged upon, because it is a conviction of the utility of the science, that can alone recommend it to attentive and persevering study. It may be proper to point out, in detail, a few of its more striking applications:

I. The art which is, of all others, the most interesting, from its subserviency to wants that are interwoven with our nature, is AGRICULTURE, or the art of obtaining, from the earth, the largest crops of useful vegetables at the smallest expense.

The vegetable kingdom agrees with the animal one, in the possession of a living principle. Every individual of this kingdom is regularly organized, and requires for its support an unceasing supply of food, which is converted, as in the animal body, into substances of various forms and qualities. Each plant has its periods of growth, health, disease, decay, and death; and is affected, in most of these particulars, by the varying condition of external circumstances. A perfect state of agricultural knowledge would require therefore, not only a minute acquaintance with the structure and economy of vegetables, but with the nature and effects of the great variety of external agents, that contribute to their nutriment, or influence their state of health and vigour. It can hardly be expected, that the former attainment will ever be generally made by practical farmers; and it is in bringing the agriculturist acquainted with the precise composition of soils and manures, that chemistry promises the most solid advantages. Indeed, any knowledge that can be acquired on this subject, without the aid of chemistry, must be vague and indistinct, and can neither enable its possessor to produce an intended effect with certainty, nor be communicated to others in language sufficiently intelligible. Thus we are told, by

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Mr. Arthur Young, that, in some parts of England, any loose clay is called marl, in others marl is called chalk, and in others, clay is called loam. From so confused an application of terms, all general benefits of experience in agriculture must be greatly limited.

Chemistry may, to agriculturists, become a universal language, in which the facts, that are observed in this art, may be so clothed, as to be intelligible to all ages and nations. It would be desirable, for example, when a writer speaks of clay, loam, or marl, that he should explain his conception of these terms, by stating the chemical composition of each substance expressed by them. For, all the variety of soils and manures, and all the diversified productions of the vegetable kingdom, are capable of being resolved, by chemical analysis, into a small number of elementary ingredients. The formation of a well defined language, expressing the proportion of these elements in the various soils and manures, now so vaguely characterized, would give an accuracy and precision, hitherto unknown, to the experience of the tillers of the earth.

It has been said, by those who contend for pure empiricism in the art of agriculture, that it has remained stationary, notwithstanding all improvements in the sciences, for more than two thousand years. "To refute this assertion," says Mr. Kirwan, " we need only compare the writings of Cato, Columella, or Pliny, with many modern tracts, or still better, with the modern practice of our best farmers."-" If the exact connexion of effects with their causes," he adds, "has not been so fully and extensively traced in this, as in other subjects, we must attribute it to the peculiar difficulty of the investigation. In other subjects, exposed to the joint operation of many causes, the effect of each, singly and exclusively taken, may be particularly examined, and the experimenter may work in his laboratory, with the object always in his view. But the secret processes of vegetation take place in the dark, exposed to the various and indeterminable influences of the atmosphere, and require, at least, half a year for their completion. Hence, the difficulty of determining on what peculiar circumstance success or failure depends; for, the diversified experience of many years can alone afford a rational foundation for solid, specific conclusions."\*

<sup>\*</sup> See Kirwan on Manures.

II. To those who study MEDICINE as a branch of general science. or with the more important view of practical utility, chemistry may be recommended with peculiar force and propriety.—The animal body may be regarded as a living machine, obeying the same laws of motion as are daily exemplified in the productions of human art. The arteries are long, flexible, and elastic canals, admitting, in some measure, the application of the doctrine of hydraulics; and the muscles are so many levers, of precisely the same effect with those which are employed to gain power in mechanical contrivances. But there is another view, in which, with equal justice, the living body may be contemplated. It is a laboratory, in which are constantly going forward processes of various kinds, dependent on the operation of chemical affinities. The conversion of the various kinds of food into blood, a fluid of comparatively uniform composition and qualities; the production of animal heat by the action of the air on that fluid, as it passes through the lungs; and the changes, which the blood afterwards undergoes in its course through the body,—are all, exclusively, subjects of chemical enquiry. To these, and many other questions of physiology, chemistry has of late years been applied with the most encouraging success; and it is to a long continued prosecution of the same plan, that we are to look for a system of physiological science, which shall derive new vigour and lustre from the passing series of years.

It must be acknowledged, however, as has been observed by Sir H. Davy,\* that the connexion of chemistry with physiology has given rise to some visionary and seductive theories; yet even this circumstance has been useful to the public mind, in exciting it by doubt, and in leading it to new investigations. A reproach, to a certain degree just, has been thrown upon those doctrines known by the name of the chemical physiology; for, in the applications of them, speculative philosophers have been guided rather by the analogies of words than of facts. Instead of endeavouring slowly to lift up the veil, which conceals the wonderful phenomena of living nature; full of ardent imaginations, they have vainly and presumptuously attempted to tear it asunder."

<sup>\*</sup> In his excellent "Discourse, Introductory to a Course of Lectures," &o, London. Johnson. 1802.

III. There is an extensive class of arts, forming, when viewed collectively, a great part of the objects of human industry, which do not, on a loose and hasty observation, present any general principle of dependency or connexion. But they appear thus disunited, because we have been accustomed to attend only to the productions of these arts, which are, in truth, subservient to widely different purposes. Who would conceive, for instance, that iron and common salt; the one a metal, the use of which results from its hardness, ductility, and malleability; the other a substance, chiefly valuable from its acting as a preservative and seasoner of food,—are furnished by arts alike dependent on the general principles of chemistry? The application of science, in discovering the principles of these arts, constitutes what has been termed Economical Chemistry; amongst the numerous objects of which, the follow-lowing stand most distinguished:

1st. Metallurgy, or the art of extracting metals from their ores, comprehending that of Assaying, by which we are enabled to judge, from the composition of a small portion, of the propriety of working large and extensive strata. To the metallurgist, also, belong the various modifications of the metals when obtained, and the union of them together, in different proportions, so as to afford compounds adapted to particular uses .- Throughout the whole of this art, much practical knowledge may be suggested by attention to the general doctrines of chemistry. The artist may receive useful hints respecting the construction of furnaces for the fusion of ores and metals; the employment of the proper fluxes; the utility of the admission or exclusion of air; and the conversion of the refuse of his several operations to useful purposes. When the metals have been separated from their ores, they are to be again subjected to various chemical processes. Cast or pig iron is to be changed into the forms of wrought or malleable iron and of steel. Copper, by combination with zinc or tin, affords the various compounds of brass, pinchbeck, bell-metal, gun-metal, &c. Even the art of printing owes something of its present unexampled perfection to the improvement of the metal of types.

2d. Chemistry is the foundation of those arts that furnish us with saline substances, an order of bodies highly useful in the business of common life. Among these, the most conspicuous are, sugar in all its various forms; the vegetable and mineral alkalies,

known in commerce by the names of potash, pearlash, and barilla; common salt; green and blue vitriol, and alum; nitre or saltpetre; sugar of lead; borax; and a long catalogue, which it is needless to extend farther.

3d. The manufacturer of glass, and of various kinds of pottery and porcelain, should be thoroughly acquainted with the nature of the substances he employs: with their fusibility, as affected by difference of proportion, or by the admixture of foreign ingredients; with the means of regulating and measuring high degrees of heat; with the principles on which depend the hardness of his products, and their fitness for bearing the vicissitudes of heat and cold; and with the chemical properties of the best adapted colors and glazing.—Even the humble art of making bricks and tiles has received from the chemical knowledge of Bergman, the addition of several interesting facts.

4th. The preparation of various kinds of fermented liquors, of wine, and ardent spirits, is intimately connected with chemical principles. Malting, the first step in the production of some of these liquors, consists in the conversion of part of the grain into saccharine matter, essential in most instances to the success of the fermentative change. To acquire a precise acquaintance with the circumstances, that favour or retard the process of fermentation, no small share of chemical knowledge is required. The brewer should be able to ascertain, and to regulate exactly, the strength of his infusions, which will vary greatly when he has seemingly followed the same routine. He should be aware of the influence of minute changes of temperature in retarding or advancing fermentation; of the means of promoting it by proper ferments; and of the influence of the presence or exclusion of atmospherical air. A complete acquaintance with the chemical princi. ples of his art, can hardly fail to afford him essential aid in its practice.

The production of ardent spirits is only a sequel of the vinous fermentation, and is, therefore, alike dependent on the doctrines of chemistry.

5th. The arts of bleaching, dyeing and printing, are, throughout, a tissue of chemical operations. It is not unusual to hear the new mode of bleaching distinguished by the appellation of the

chemical method; but, it is in truth, not more dependant on the principles of this science, than the one which it has superceded, nor than the kindred arts of dyeing and printing. In the instance of bleaching, the obligation due to the speculative chemist is universally felt and acknowledged. But the dyer and the printer have yet to receive from the philosopher some splendid invention, which shall command their respect, and excite their attention to chemical science. From purely speculative men, however, much less is to be expected, than from men of enlightened experience, who endeavour to discover the design and reason of each step in the processes of their arts, and fit themselves for more effectual observation of particular facts, by diligently possessing themselves of general truths.

The objects of inquiry that present themselves to the dyer and printer, are of considerable number and importance. The preparation of goods for the reception of colouring matter; the application of the best bases, or means of fixing fugitive colours; the improvement of colouring ingredients themselves; and the means of rendering them permanent, so that they shall not be affected by soap, or by the accidental contact of acids or other corrosive bodies; are among the subjects of chemical investigation. It is the business of the dyer, therefore, to become a chemist; and he may be assured that, even if no brilliant discovery should be the reward of the acquisition, he will yet be better fitted by it for conducting common operations, with certain and unvaried success.

6th. The tanning and preparation of leather are processes strictly chemical, which were involved in mystery, till they were reduced to well established principles by the researches of Seguin, and by the subsequent experiments of Davy. In this, as in most other examples, the application of science to the practical improvement of an art, has to encounter the obstacles of ignorance and prejudice. But the interests of men are sure finally to prevail; and the most bigotted attachment to established forms must give place to the clearly demonstrated utility of new practices. Such a demonstration is generally furnished by some artist of more enlightened views than his neighbours, who has the spirit to deviate from ordinary rules; and thus becomes (not unfrequently with some personal sacrifice) a model for the imitation of others, and an important benefactor of mankind.

Many other chemical arts might be enumerated; but enough, I trust, has been said, to evince the connexion between practical skill and the possession of scientific knowledge. I shall now proceed to develope the plain, on which the following course of instruction will be conducted.

There are two methods of delivering the general doctrines of chemistry, and the facts connected with them. The one consists in a historical detail of the gradual progress of the science; and, in pursuing this plan, we follow the natural progress of the human mind, ascending from particular facts to the establishment of general truths. But a strong objection to its adoption is, that we are thus led into a minuteness of detail, which is ill suited to the plan of elementary instruction. In the other mode of arrangement, we neglect wholly the order of time in which facts were discovered, and class them under general divisions so framed as to assist the mind in apprehending and retaining the almost infinite variety of particular truths.

In a classification of the objects of chemistry, we may either begin with those substances, which are deemed to be simple, and proceed gradually to the more complicated:—or we may take bodies, as they are usually presented to us, and arrange them according to the resemblances of their external characters; making the development of their composition a subordinate part of the plan. To the former, or synthetic method, there is this strong objection,-that as we are probably still very remote from a knowledge of the true elements of matter, it must be liable, in the progress of science, to frequent and fundamental changes. been found necessary, for example, in consequence of Sir H. Davy's discoveries, to remove the fixed alkalies and the earths from the class of simple to that of compound bodies. Besides, it may be urged, where are we to place those substances, which have his therto resisted all attempts at their analysis, and yet have a striking resemblance, in natural characters, to the bodies with which they are already associated? For these reasons it appears to me, that one arrangement is preferable to another, on no other ground, than as it is better adapted for communicating a knowledge of the subject; for all must be equally remote from that perfection, which cannot be considered as attained, till the science of chemistry shall no longer be capable of improvement.

The order, which I have adopted as most eligible, is to commence with those facts, which lead most directly to the establishment of general principles. Attraction or affinity, as the great cause of all chemical changes, and as admitting of illustration by phenomena that are sufficiently familiar, has a primary claim to consideration. Next to that of attraction, the influence of Heat. over the forms and properties of bodies, is the most generally observed fact; and as heat is a power, which is constantly opposed to that of affinity, there is the more propriety in contrasting their operation. With heat, Light also, as a repulsive agent, is frequently associated, and Electricity belongs to the same class of powers. But as the action of electricity consists, chiefly, in effecting the disunion of chemical compounds, I have removed it from that place in the system, which seems naturally to belong to For before we can understand the general laws of electrochemical agency, it is necessary to know something of oxygen and a few of the inflammable bodies; nor can the theory of the excitation of galvanic electricity be made at all intelligible, without this previous knowledge.

.The phenomena of heat, and the laws deduced from them, conduct us naturally to the great source of that fluid, which will be traced to a class of bodies agreeing, in mechanical properties, with the air of our atmosphere, and called airs or gases. These gases, we shall find, consist partly of gravitating matter, and partly of an extremely subtile fluid, which impresses on our organs the sensation of heat, and is called caloric\*. When the ponderable ingredients, usually called the bases, of these gases, combine together, or with other bodies, caloric is given out, and new compounds are generated. It is on the possession or absence of the property of decomposing one of them, oxygen gas, that a comprehensive division has been made of bodies into combustible and incombustible. In this view of the subject, combustion necessarily implies the fixation of oxygen; but the term has lately been extended to every case of energetic chemical combination, which is accompanied with heat and light. With oxygen, chlorine possesses such numerous and close analogies, that it can only with propriety be placed along with that element, in the class of che-

<sup>\*</sup> Light and electricity are probably, also, constituents of the gases.

mical agents, which have been called supporters of combustion. Iodine is, also, entitled to the same rank; and it is for purposes of convenience, and with the view of giving a more complete history of it, that I have placed it in a different part of the work.

The next division of bodies, that claim our attention, includes those, which are formed either by the mixture or union of the simple gases or of their bases. Thus oxygen and nitrogen gases compose atmospheric air; and hydrogen and oxygen, water. Nitrogen and hydrogen, by their union, afford ammonia; and with this fluid the fixed alkalies are naturally associated. The detail of properties belonging to the alkalies and earths is, indeed, a necessary preliminary to that of the acids, the most important quality of which is, that they constitute, with the alkalies and earths, an extensive class of neutral salts. The consideration of the bases of the alkalies and earths has been made to follow that of the bodies themselves, because these bases are the products of refined and complicated operations, which could scarcely have been otherwise understood. The fixed alkalies, also, precede the volatile ones, on account of the singular effects of potassium on ammonia.

The next class of compounds is that of Acids. With each of these I have connected the history of its base, when known; for as several of these bodies have already lost, and others appear likely to lose, their title to be considered as elementary, it becomes merely a question of convenience where they should be placed. In treating of the acids, their relation will be traced to those bodies only which have already been described; for it would be unseasonable to detail their action on metals, till that class of substances has been specifically discussed.

Having dismissed the consideration of such elementery bodies, as are distinguished by affording acids when combined with oxygen, of the properties of acids thus generated, and of the compounds afforded by the union of acids with alkalies; an important division of elementary substances will next claim our attention, viz. the Metals.

The class of bodies, it is usual to introduce at a much earlier period: but I have adopted a different order, from the consideration, that, with the previous knowledge of the constitution and qualities of acids, the history of the metals may be made much more complete; and, especially, that all the various modes and

phenomena of their combination with oyxgen and chlorine may be more distinctly explained. The more complex productions of the vegetable and animal kingdoms will be the last step in our progress through the chemical arrangement of bodies; and the concluding part of the work will be occupied with practical rules, derived from the facts and principles explained in the course of it, and applicable to the solving of various interesting problems in chemical analysis.

## **ELEMENTS**

OF

## EXPERIMENTAL CHEMISTRY.

PART I.

## CHAPTER L

OF A CHEMICAL LABORATORY AND APPARATUS.

A CHEMICAL laboratory, though extremely useful, and even essential, to all who embark extensively in the practice of chemistry, either as an art, or as a branch of liberal knowledge, is by no means required for the performance of those simple experiments, which furnish the evidence of the fundamental truth of the science. A room that is well lighted, easily ventilated, and destitute of any valuable furniture, is all that is absolutely necessary for the purpose. It is even adviseable, that the construction of a regular laboratory should be deferred, till the student has made some progress in the science; for he will then be better qualified to accommodate its plan

to his own peculiar views and convenience.

It is scarcely possible to offer the plan of a laboratory, which will be suitable to every person, and to all situations; or to suggest any thing more than a few rules that should be generally observed. Different apartments are required for the various classes of chemical operations. The principal one may be on the ground-floor; twenty-five feet long, fourteen or sixteen wide, and open to the roof, in which there should be contrivances for allowing the occasional escape of suffocating vapours. This will be destined chiefly for containing furnaces, both fixed and portable. It should be amply furnished with shelves and drawers, and with a large table in the centre, the best form of which is that of a double cross. Another apartment may be appropriated to the minuter operations of chemistry; such as those of precipitation on a small scale, the processes that require merely the heat of a lamp, and experiments on the gases. In a third of smaller size, may be deposited accurate balances, and other instruments of considerable nicety, which would be injured by the acid fumes that are constantly spread through a laboratory.

The following are the principal instruments that are required in chemical investigations; but it is impossible, without entering into very tedious details, to enumerate all the apparatus that should be in the possession of a practical chemist.

I. FURNACES. These may be formed either of solid brick-work, or of such materials as admit of their removal from place to place.

The directions generally laid down in elementary books of chemistry, for the construction of FIXED FURNACES, appear to me deficient in precision, and such as a workman would find it difficult to put in practice. I have, therefore, given plans and sections, in the last two plates, of the various kinds of furnaces; and in the Appendix, minute instructions will be found for erecting them\*.

The furnaces of most general utility are, 1st, the Wind Furnace, in which an intense heat is capable of being excited for the fusion of metals, &c. In this furnace, the body submitted to the action of heat, or the vessel containing it, is placed in contact with the burning fuel. Fig. 60 exhibits one of the most common construction. Fig. 61 is the section of a wind furnace; the plan of which was obligingly communicated to me by Mr. Knight, of Foster-lane, London, to whom, also, I am indebted for that represented, fig. 62. The wind furnace of Mr. Chenevix is shown by fig. 74. 2dly, The Evaporating Furnace is formed of iron plates, joined together by rabbiting, and placed over horizontal returning flues of brick. Figs. 64 and 65, are two views of this furnace as recommended by Mr. When evaporation is performed by the naked fire, the vessel may be placed on the top of the furnace, fig. 60 or 61; and when effected through the intervention of a water bath, a shallow kettle of water, in which is placed the evaporating dish and its contents, may be set in the same situation. For the purposes of evaporating liquids, and drying precipitates on a small scale, at a temperature not exceeding 2120 Faht, a convenient apparatus is represented by fig. 27. 3dly, The plan of a Reverberatory Furnace is exhibited by figs. 66, 67, and 68. 4thly, The Furnace for distilling by a Sand Heat is constructed by setting upon the top of the brick-work, fig. 60, the iron pot, fig. 71; a door being made in the side of the furnace for introducing fuel. Distillation by the naked fire is performed with the wind furnace, figs. 62, 63. 5thly, The Cupelling, or Enamelling Furnace, is shown by figs. 69, 70.

Portable furnaces, however, are amply sufficient for all the purposes of the chemical student, at the outset of his pursuit. The one which I prefer is that shown by figs. 58 and 59. It was originally contrived, I believe, by Mr. Schmeisser; and is made, with considerable improvements, and sold by Mr. Knight, and by other dealers in chemical apparatus. Its size is so small, that it may be set on a table, and the smoke may be conveyed by an iron pipe, into the chimney of the apartment. In the furnace, as it is usually sold, the chimney, adapted for distillation with a sand heat, passes di-

<sup>\*</sup> See the Description of the 7th and 8th plates in the Appendix.

<sup>†</sup> See his Mineralogy, Tab. iii. and iv.

rectly through the sand-bath, the form of which is necessarily altered, from the common to a very inconvenient one. I have found it a great improvement to make the aperture for the chimney at k. This allows us to have a sand-bath of the usual shape, as shown by fig. 59; or even to place evaporating dishes, or a small boiler, on the top of the furnace. The aperture may be closed by a stopper, when we dispose the furnace as shown by fig. 28. Dr. Black's furnace is generally made of a larger size, and is adapted to operations on a more considerable scale. (See figs. 72 and 73.) Both these furnaces are constructed of thin iron plates, and are lined with fire-clay. They will be minutely described in the references to the plates.

For the purpose of exciting a sudden heat, and of raising it to great intensity, nothing can be better adapted than a very simple, cheap, and ingenious furnace, contrived by Mr. Charles Aikin, fig. 55. It is formed out of pieces of black-lead melting pots, in a manner to be described in the Appendix, and is supplied with air by a pair of double bellows, d. By a slight alteration, this furnace may occasionally be employed for the operation of cupelling. (See

fig. 57.)

II. For containing the materials, which are to be submitted to the action of heat in a wind furnace, vessels called CRUCIBLES are em-They are most commonly made of a mixture of fire-clay and sand, occasionally with the addition of plumbago, or black lead. The Hessian crucibles are best adapted for supporting an intense heat without melting; but they are liable to crack when suddenly heated or cooled. The porcelain ones, made by Messrs. Wedgwood, are of much purer materials, but are still more apt to crack on sudden changes of temperature; and, when used, they should, therefore, be placed in a common crucible of larger size, the interval being filled with sand. The black lead crucibles resist very sudden changes of temperature and may be repeatedly used; but they are destroyed when some saline substances (such as nitre) are melted in them, and are consumed by a current of air. For certain purposes, crucibles are formed of pure silver or platina. Their form varies considerably, as will appear from inspecting plate vi. figs. 49, 50, 51, and 54. It is necessary, in all cases, to raise them from the bars of the grate, by a stand, fig. 53, a or b. For the purpose of submitting substances to the continued action of a red heat, and with a considerable surface exposed to the air, the hollow arched vessel, with a flat bottom, fig. 52, termed a muffle, is commonly used. In fig. 69. d, e, the muffle is shown, placed in a furnace for use.

III. Evaporating vessels should always be of a flat shape, so as to expose them extensively to the action of heat. (See a section of one, fig. 12.) They are formed of glass, of earthen ware, and of various metals. Those of glass are with difficulty made sufficiently thin and are often broken by change of temperature; but they have a great advantage in the smoothness of their surface, and in resisting the action of most acid and corrosive substances. Evaporating vessels of porcelain, or Wedgwood's ware, are next in utility, are less costly, and less liable to be cracked. They are made both of glazed

and unglazed ware. For ordinary purposes the former are to be preferred; but the unglazed should be employed when great accuracy is required, since the glazing is acted on by several chemical substances. Evaporating vessels of glass, or porcelain, are generally bedded, up to their edge, in sand (see fig. 65;) but those of various metals are placed immediately over the naked fire. When the glass or porcelain vessel is very thin, and of small size, as a watch glass for example, it may be held by means of a small prong, represented under fig. 12; or it may be safely placed on the ring of the brass stand, plate i. fig. 13, and the flame of an Argand's lamp, cautiously regulated, may be applied beneath it. A lamp thus supported, so as to be raised or lowered, at pleasure, on an upright pillar, to which rings, of various diameters, are adapted, will be found extremely useful; and, when a strong heat is required, it is adviseable to employ a lamp, furnished with double concentric wicks. A lamp for burning spirit of wine will, also, be found very convenient, especially if provided (as they now generally are) with a glass cap to cover the wick when not in use, which, being fitted by grinding, prevents the waste of the spirit by evaporation.

IV. In the process of evaporation, the vapour for the most part is allowed to escape; but of certain chemical processes, the collection of the volatile portion is the principal object. This process is termed distillation. It is performed in vessels of various forms and materials. The common still is so generally known, that a representation of it in the plates was deemed unnecessary\*. It consists of a vessel, generally of copper, shaped like a tea-kettle, but without its spout and handle. Into the opening of this vessel, instead of a common lid, a hollow moveable head is fixed, which ends in a narrow, open pipe. This pipe is received into another tube of lead, which is twisted spirally, and fixed in a wooden tub, so that it may be surrounded by cold water. (Fig. 40, dd.) When the apparatus is to be used, the liquid intended to be distilled is poured into the body of the still, and the head is fixed in its place, the pipe, which terminates it, being received into the leaden worm. The liquid is raised into vapour, which passes into the worm, is there condensed by the surrounding cold water and flows out at the lower extremity.

rounding cold water and nows out at the lower extremity.

The common still, however, can only be employed for volatilizing substances that do not act on copper, or other metals, and is, therefore, limited to very few operations. The vessel, fig. 2, is of glass, or earthen ware, and is also intended for distillation. It is termed an alembic, and consists of two parts; the body a for containing the materials, and the head b by which the vapour is condensed; the pipe c conveying it to a receiver. Vessels, termed retorts, however, are more generally used. Fig. 1, a shows the common form, and fig. 13, a represents a stoppered, or tubulated retort. Retorts are made of glass, of earthen ware, or of metal. When a liquid is to be added at distant intervals during the process, the best contrivance is that shown fig. 26, a, consisting of a bent tube, with a funnel at

<sup>\*</sup> See Aikin's Chem. Dict. pl. ii, fig. 31.

the upper end. When the whole is introduced at first, it is done either through the tubulure, or, if into a plain retort, through the

funnel, fig. 10.

To the retort, a receiver is a necessary appendage; and this may either be plain, fig. 1, b, or tubulated, as shown by the dotted lines at c. To some receivers a pipe is added (fig. 13, b,) which may enter partly into a bottle beneath. This vessel, which is principally useful for enabling us to remove the distilled liquid, at different periods of the process, is termed a quilled receiver. For some purposes, it is expedient to have the quilled part accurately ground to the neck of the bottle, c, which would then be furnished with a tubulure, or second neck, having a ground stopper, and should be provided, also, with a bent tube, to be occasionally applied, for conveying away any gases that may be produced. The condension of the vapour is much facilitated, by lengthening the neck of the retort with an adopter (fig. 11,) the wider end of which slips over the retort neck, while its narrow extremity is admitted into the mouth of the receiver (See fig. 63.)

Heat may be applied to the retort in several modes. When the vessel is of earthen ware, and when the distilled substance requires a strong heat to raise it into vapour, the naked fire is applied, as shown fig. 63. Glass retorts are generally placed in heated sand (fig. 59); and, when of a small size, the flame of an Argand's lamp,

cautiously regulated, may be conveniently used (fig. 13.)

In several instances, the substance raised by distillation is partly a condensible liquid, and partly a gas, which is not condensed till it is brought into contact with water. To effect this double purpose, a series of receivers, termed Woulfe's Apparatus, is employed. The first receiver (b, fig, 30) has a right-angled glass tube, open at both ends, fixed into its tubulure; and the other extremity of the tube is made to terminate beneath the surface of distilled water, contained, as high as the horizontal dotted line, in the three-necked bottle c. From another neck of this bottle, a second pipe proceeds, which ends, like the first, under water, contained in a second bottle d. To the central neck a straight tube, open at both ends, is fixed, so that its lower end may be a little beneath the surface of the liquid. Of these bottles any number may be employed that is thought necessary.

The materials being introduced into the retort, the arrangement completed, and the joints secured in the manner to be presently described, the distillation is begun. The condensible vapour collects in a liquid form in the balloon b, while the evolved gas passes through the bent pipe, beneath the surface of the water in c, which continues to absorb it till saturated. When the water of the first bottle can absorb no more, the gas passes, uncondensed, through the second right angled tube, into the water of the second bottle, which, in its turn, becomes saturated. Any gas that may be produced, which is not absorbable by water, escapes through the bent tube a, and may

be collected, if necessary.

Supposing the bottles to be destitute of the middle necks, and, consequently, without the perpendicular tubes, the process would be liable to be interrupted by an accident: for if, in consequence of a diminished temperature, an absorption or condensation of gas should take place, in the retort a, and, of course, in the balloon b, it must necessarily ensue that the water of the bottles c and d would be forced, by the pressure of the atmosphere, into the balloon, and possibly into the retort; but with the addition of the central tubes, a sufficient quantity of air rushes through them to supply any accidental vacuum. This inconvenience, however, is still more conveniently obviated by Welther's tube of safety (fig. 31, b,) which supersedes the expediency of three-necked bottles. The apparatus being adjusted, as shown by the figure, a small quantity of water is poured into the funnel, so as to about half fill the ball b. When any absorption happens, the fluid rises in the ball, till none remains in the tube, when a quantity of air immediately rushes in. On the other hand, no gas can escape, because any pressure from within is instantly followed by the formation of a high column of liquid in the perpendicular part, which resists the egress of gas. This ingenious invention I can recommend, from ample experience of its utility.

Very useful alterations in the construction of Woulfe's apparatus have been contrived also by Mr. Pepys and Mr. Knight. That of the former is shown (fig. 32,) where the balloon b is surmounted by a vessel accurately ground to it, and furnished with a glass valve, resembling that affixed to Nooth's apparatus. This valve allows gas to pass freely into the vessel c, but prevents the water which it contains from falling into the balloon. Mr. Knight's improvement is described, and represented in a plate, in the Philosophical Maga-

zine, vol. xx\*.

When a volatile substance is submitted to distillation, it is necessary to prevent the escape of the vapour through the junctures of the vessels; and this is accomplished by the application of LUTES. The most simple method of confining the vapour, it is obvious, would be to connect the places of juncture accurately together by grinding; and accordingly the neck of the retort is sometimes ground to the mouth of the receiver. This, however, adds too much to the expense of apparatus to be generally practised.

When the distilled liquor has no corrosive property (such as water, alcohol, ether, &c.) slips of moistened bladder, or of paper, or linen, spread with flour paste, white of egg, or mucilage of gum arabic, sufficiently answer the purpose. The substance which remains, after expressing the oil from bitter almonds, and which is sold under the name of almond-meal, or powder, forms a useful lute, when mix-

ed, to the consistency of glaziers' putty, with water or mucilage.

<sup>\*</sup> Another modification of this apparatus, by Dr. Murray, is represented in Nich. Journ. 8vo. vol. iii. or in Murray's System of Chemistry, vol. i. pl. v. fig. 40. Fig. 41 of the same plate exhibits a cheap and simple form of this apparatus, contrived by the late Dr. Hamilton, and depicted originally in his translation of Berthollet on Dyeing. Mr. Burkit's improvement of this apparatus may be seen in Nicholson's Journal, 4to. vol. v. 349.

For confining the vapour of acid, or highly corrosive substances, the fat lute is well adapted. It is formed by beating perfectly dry and finely sifted tobacco pipe-clay, with painters' drying oil, to such a consistence that it may be moulded by the hand. The same clay, beat up with as much sand as it will bear, without losing its tenacity, with the addition of cut tow, or of horse-dung, and a proper quantity of water, furnishes a good lute, which has the advantage of resisting a considerable heat, and is applicable in cases where the fat lute would be melted or destroyed. Various other lutes are recommended by chemical writers; but the few that have been enumerated I

find to be amply sufficient for every purpose.

On some occasions, it is necessary to protect the retort from too sudden changes of temperature, by a proper coating. For glass retorts, a mixture of moist common clay, or loam, with sand, and cut shreds of tow or flax, may be employed. If the distillation be performed by a sand heat, the coating needs not be applied higher than that part of the retort which is bedded in sand; but if the process be performed in a wind furnace (fig. 63), the whole body of the retort, and that part of the neck also which is exposed to heat, must be carefully coated. To this kind of distillation, however, earthen retorts are better adapted; and they may be covered with a composition originally recommended by Mr. Willis. Two ounces of borax are to be dissolved in a pint of boiling water, and a sufficient quantity of slaked lime added, to give it the thickness of cream. This is to be applied by a painter's brush, and allowed to dry. Over this a thin paste is afterwards to be applied, formed of slaked lime and common linseed-oil, well mixed and perfectly plastic. In a day or two the coating will be sufficiently dry to allow the use of the retort.

For joining together the parts of iron vessels, used in distillation, a mixture of the finest China clay, with solution of borax, is well adapted. In all cases, the different parts of any apparatus made of iron should be accurately fitted by boring and grinding, and the above lute is to be applied to the part which is received into an aperture. This will generally be sufficient without any exterior luting; otherwise the lute of clay, sand, and flax, already described,

may be used.

In every instance, where a lute or coating is applied, it is adviseable to allow it to dry before the distillation is begun; and even the fat lute, by exposure to the air during one or two days after its application, is much improved in its quality. The clay and sand lute is perfectly useless, except it be previously quite dry. In applying a lute, the part immediately over the juncture should swell outwards, and its diameter should be gradually diminished on each side. (See fig. 13, where the luting is shown, applied to the joining of the retort and receiver.)

Beside the apparatus already described, a variety of vessels and instruments are necessary, having little resemblance to each other, in the purposes to which they are adapted. Glass vessels are requir-

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ed for effecting solution, which often requires the application of heat, and sometimes for a considerable duration. In the latter case, it is termed digestion, and the vessel, fig. 4, called a matrass, is the most proper for performing it. When solution is required to be quickly effected, the bottle, fig. 5, with a rounded bottom, may be used; or a common Florence oil flask serves the same purpose extremely well, and bears, without cracking, sudden changes of temperature. For precipitations, and separating liquids from precipitates, the decanting-jar (fig. 14), will be found useful; or, if preferred, it may be shaped as in fig. 26, f. Liquids, of different specific gravities, are separated by the vessel, fig. 3; the heavier fluid being drawn off through the cock b, and air being admitted by the removal of the stopper a, to supply its place. Glass rods, of various lengths, and spoons of the same material, or of porcelain, are useful for stirring acid and corrosive liquids; and a stock of cylindrical tubes, of various sizes, is required for occasional purposes. It is necessary also to be provided with a series of glass measures, graduated into drachms, ounces, and pints. The small tube, fig. 15, called a dropping tube, which is open at each end and blown in the middle into a ball, will be found useful in directing a fine stream of water upon the edges of a filtre, or any small object. The same purpose may, also, be very conveniently effected by fixing a piece of glass tube of small bore, two or three inches long, and bent at one end to an obtuse angle, into a hole bored in a cork, which may be used as the stopple of an eight ounce vial filled with water, fig. 25, a. On inverting the vial, and grasping the bottom part of it, the warmth of the hand expels either a few drops or a small stream of water, which may be directed upon any minute object. When the flow ceases, it may be renewed, if required, by setting the bottle, for a moment, with its mouth upwards (which admits a fresh supply of cool air), and then proceeding as before.

For the drying of precipitates, and other substances, by a heat not exceeding  $212^\circ$ , a very useful apparatus is sold in London. It is represented, supported by the ring of a lamp-stand, by fig. 27. The vessel a is of sheet-iron or copper japanned and hard-soldered; c is a conical vessel of very thin glass, having a rim, which prevents it, when in its place, from entirely slipping into a; and d is a moveable ring, which keeps the vessel c in its place. When the apparatus is in use, water is poured into a about as high as the dotted line; the vessel c, containing the substance to be dried, is immersed in the water, and secured by the ring d; and the whole apparatus set over an Argand's lamp. The steam escapes by means of the chimney b, through which a little hot water may be occasionally poured, to supply the waste by evaporation. By changing the shape of c to the segment of a sphere, still retaining the rim, I have

found it a most convenient vessel for evaporating fluids.

Accurate beams and scales, of various sizes, with corresponding weights, some of which are capable of weighing several pounds, while the smaller size ascertains a minute fraction of a grain, are essential instruments in the chemical laboratory. So also are mor-

tars of different materials, such as of glass, porcelain, agate, and metal. Wooden stands, of various kinds, for supporting receivers, should be provided\*. For purposes of this sort, and for occasionally raising to a proper height any article of apparatus, a series of blocks, made of well seasoned wood, eight inches (or any other number) square, and respectively, eight, four, two, one, and half an inch in thickness, will be found extremely useful; since, by combining them in different ways, thirty-one different heights may be obtained.

The blow-pipe is an instrument of much utility in chemical researches. A small one, invented by Mr. Pepys, with a flat cylindrical box for condensing the vapour of the breath, and for containing caps, to be occasionally applied with apertures of various sizes, is perhaps the most commodious formt. One of a much smaller size, for carrying in the pocket, has been contrived by Dr. Wollaston‡. A blow-pipe, which is supplied with air from a pair of double bellows, worked by the foot §, may be applied to purposes that require both hands to be left at liberty, and will be found useful in blowing glass, and in bending tubes. The latter purpose, however, may be accomplished by holding them over an Argand's lamp with double wicks. Occasionally, when an intense heat is required, the flame of the blow-pipe, instead of being supported by the mouth, may be kept up by a stream of oxygen gas, expelled from a bladder or from a gas-holder ||. The blow-pipe invented by Mr. Brooke, consists of a small square box of copper or iron, into which air is forced by a condensing syringe, and from which it is suffered to rush, through a tube of very small aperture, regulated by a stop-cock, against the flame of a lamp or candle ¶. By means of a screw added to the syringe, the receiver may be filled with oxygen gas, or, as will be described in chap. v. sect. 5, with a mixture of hydrogen and oxygen gases. Blow pipes on this construction may be had of Mr. Newman, and of most of the other makers of philosophical instru-

In the course of this work, various other articles of apparatus will be enumerated, in detailing the purposes to which they are adapted, and the principles on which they are constructed. It must be remembered, however, that it is no part of my object to describe every ingenious and complicated invention, which has been employed in the investigation of chemical science: but merely to assist the student in attaining apparatus for general and ordinary purposes. For such purposes, and even for the prosecution of new and important

- \* See Aikin's Chem. Dict. pl. iv. fig. 59, e.
- † See Aikin's Chem. Dict. pl. vii. fig. 71, 72,73.
- ‡ It is described in Nich. Journ. xv. 284.
- § Phil. Mag. xliii. 280.
- || See a representation of the apparatus for this purpose, in the Chemical Conversations. pl. ix.
  - Thomson's Annals, vii, 367; or, Journal of Science and the Arts, i. 65,

inquiries, very simple means are sufficient; and some of the most interesting chemical facts may be exhibited and even ascertained, with the aid merely of Florence flasks, of common vials, and of wine glasses. In converting these to the purposes of apparatus, a considerable saving of expense will accrue to the experimentalist; and he will avoid the encumbrance of various instruments, the value

of which consists in show, rather than in real utility.

In the selection of experiments, I shall generally choose such as may be undertaken by persons not possessed of an extensive chemical apparatus. On some occasions, however, it may be necessary, in order to complete the series, that others should be included, requiring, for their performance, instruments of considerable nicety. The same experiment may, perhaps, in a few instances, be repeatedly introduced in illustrations of different principles; but this repctition will be avoided as much as possible. Each experiment will be preceded by a brief enunciation of the general truth which it is intended to illustrate.

## CHAPTER II:

#### OF CHEMICAL AFFINITY.

All bodies, composing the material system of the universe, havea mutual tendency to approach each other, whatsoever may be the distances at which they are placed. The operation of this force extends to the remotest parts of the planetary system, and is one of the causes that preserve the regularity of their orbits. The smaller bodies, also, that are under our more immediate observation, are influenced by the same power, and fall to the Earth's surface when not prevented by the interference of other forces. From these facts, the existence of a property has been inferred, which has been called attraction, or more specifically, the attraction of gravitation. Its nature is entirely unknown to us; but some of its laws have been investigated, and successfully applied to the explanation of phenome-Of these, the most important are, that the force of gravity acts on bodies directly in proportion to the quantity of matter in each; and that it decreases in the reciprocal proportion of the squares of the distances.

From viewing bodies in the aggregate, we may next proceed to contemplate them as composed of minute particles. Of the nature of these particles, we have no satisfactory evidence. It is probable that they consist of solids, which are incapable of mechanical division, but are still possessed of the dimensions of length, breadth, and thickness. In simple bodies, the particles must be all of the same nature, or homogeneous. In compound bodies, we are to understand, by the term particles, the smallest parts into which bodies can be resolved without decomposition. The word atom has of late been revived, to denote both these kinds of particle; and we may,

therefore, speak, with propriety, of simple atoms and of compound atoms. When two atoms of different kinds unite to form a third or compound atom, we may term the two first component atoms; and if these have not been decomposed, they may be called elementary or primary atoms.

The atoms or particles of bodies are also influenced by the force of attraction, but not unless when placed in apparent contact. Hence a distinction has been made between gravitation, and that kind of attraction which is effective only at insensible distances. The latter has been called contiguous attraction or affinity; and

it has been distinguished, as it is exerted between particles of matter, of the same kind, or between particles of a different kind.

By the affinity of aggregation the cohesive affinity, or more simply cohesion, is to be understood that force or power, by which particles or atoms of matter of the same kind attract each other, the only effect of this affinity being an aggregate or mass. Thus a lump of copper may be considered as composed of an infinite number of minute particles or integrant parts, each of which has precisely the same properties, as those that belong to the whole mass. These are united by the force of cohesion. But if the copper be combined with another metal (such as zinc), we obtain a compound (brass), the constituent parts of which, copper and zinc, are combined by the power of chemical affinity. In simple bodies, therefore, cohesion is the only force exerted between these particles. But in compound bodies, we may distinguish the force, with which the component atoms are united, from that which the compound atoms exert towards each other; the former being united by chemical affinity, and the latter by the cohesive attraction.

#### SECTION I.

# Of Cohesion, Solution, and Crystallization.

The cohesive affinity is a property, which is common to a great variety of bodies. It is most strongly exerted in solids; and in these it is proportionate to the mechanical force required for effecting their disunion. In liquids, it acts with considerably less energy; and in aëriform bodies we have no evidence that it exists at all; for their particles, as will afterwards be shown, are mutually repulsive, and, if not held together by pressure, would probably separate to immeasureable distances. Its force is not only different among different bodies, but in various states of the same body. Thus in the cohesion of certain metals (steel for instance), important changes are produced by the rate of cooling, by hammering, and by other mechanical operations. Water, also, in a solid state, has considerable cohesion, which is much diminished when it becomes liquid, and is entirely destroyed when it is changed into vapour.

The most important view, in which the chemist has to consider cohesion, is that of a force either counteracting or modifying chemical affinity; for the more strongly the particles of any body are united by this power, the less are they disposed to enter into combination with other bodies. In many cases, a very powerful affinity existing between two substances may be rendered wholly inefficient, by the strong cohesion of one or both of them. Hence it has been received as an axiom, that the affinity of composition is inversely proportionate to the cohesive affinity. To the language however in which this axiom is expressed, it has been justly objected, that it implies an accuracy of proportion between the forces of cohesion and of chemical affinity, which cannot be proved to exist; since all that can truly be affirmed is, in general terms, that the affinity of composition is less effective, as the attraction of cohesion is stronger.

The cohesion of bodies may be overcome, 1st, by mechanical operations, as by rasping, grinding, pulverising, and other modes of division which are generally employed as preliminary steps to chemical processes. In some instances, even a minuter division of bodies is necessary, than can be accomplished by mechanical means; and resource is then had to precipitation. Silica, for example, in the state of rock crystal, may be boiled for a long time in liquid potash, without any appearance of chemical action. It may even be bruised to the finest powder, without being rendered sensibly soluble. But when first precipitated from a state of chemical solution, it is readily

dissolved by that menstruum.

2dly. Cohesion may be contracted by heat, applied so as to melt one or both of the bodies, if fusible; or to raise them into vapour, if volatile. Lead and sulphur contract no union, till one or both of them is melted by heat. Arsenic and sulphur are united most effectually, by bringing them into contact, when both are in a state of vapour.

3dly. Cohesion may be counteracted by solution; and this is so general a condition of chemical union, that it was formerly received as an axiom, that bodies do not act on each other, unless one or both are in a state of solution; a principle, to which the progress of che-

mical science has since discovered many exceptions.

The term solution is applied to a very extensive class of phenomena. When a solid disappears in a liquid, or when a solid or liquid is taken up by an aëriform body, if the compound exhibit perfect transparency, we have, in each instance, an example of solution. The expression is applied, both to the act of combination, and to the result of the process. When common salt, such as is used in cookery, is agitated with water, it disappears; in other words, its solution takes place; and we also term the liquid which is obtained, a solution of salt in water. This is one of the simplest cases that can be adduced, of the efficiency of chemical affinity; for solution is always the result of an affinity between the fluid and the solid which is acted upon, sufficient in force to overcome the cohesion of the solid. The affinity continues to act, until, at length, a certain point is attained, where the affinity of the solid and fluid for each other is

overbalanced by the cohesion of the solid, and the solution cannot be carried farther. This point is called saturation, and the fluid obtained is termed a saturated solution.

With respect to common salt, water acquires no increase of its solvent power by the application of heat. But there are various salts with which water may be saturated at the common temperature of the atmosphere, and will yet be capable of dissolving a still farther quantity by an increase of its temperature. When a solution, thus charged with an additional quantity of salt, is allowed to cool, the second portion of salt is deposited in a form resembling its original one.

To recover a salt from its solution, if its solubility does not vary with the temperature of the solvent, as in the instance of common salt, it is necessary to expel a portion of the fluid by heat. This constitutes the process of evaporation. If the evaporation be carried on very slowly, so that the particles of the solid may approach each other in the way best adapted to them, we obtain solid figures, of a regular shape, called crystals. The crystallization of a solid may also take place from that state of fluidity which is produced by heat. Thus several of the metals crystallize on cooling from a melted state; and some volatile bodies, as arsenic, assume, when condensed from the state of vapour, the shape of regular crystals.

In the act of separating from the water in which they were dissolved, the crystals of almost all salts carry with them a quantity of water, which is essential to the regularity of their form, and cannot be expelled without reducing them to shapeless masses. It is termed their water of crystallization. Its proportion varies in different salts; in some it is extremely small; in others it constitutes the principal part of the salt, and is even so abundant, as to liquefy them on the application of heat, producing what is called the watery fusion. The water of crystallization is retained also in different salts with very different degrees of force. Some crystals, which lose their watery ingredient by mere exposure to the atmosphere, are said to effloresce. Others, on the contrary, not only hold their water of crystallization very strongly, but even attract more; and on exposure to the atmosphere, become liquid, or deliquiate. The property itself is called deliquescence.

When two salts are contained in the same solution, which vary in their degree of solubility, and which have no remarkable attraction for each other, they may be obtained separate. For, by carefully reducing the quantity of the solvent by evaporation, the salt whose particles have the greatest cohesion, will crystallize first. If both salts are more soluble in hot than in cold water, the crystals will not appear till the liquid cools. But if one of them, like common salt, is equally soluble in hot and in cold water, crystals will appear, even during the act of evaporation. In this way we may completely separate nitre from common salt, the crystals of the latter being formed during evaporation; while those of nitre do not appear

till some time after the fluid has cooled.

Salts, which are thus deposited in regular shapes, generally adhere to the surface of the vessel containing the solution, or to any substance, such as pieces of thread or of wood, introduced for the purpose of collecting them. But a still more effectual way of inducing crystallization is to immerse, in the solution, a crystal of the same kind with that which we expect to be formed. The crystal, thus exposed, receives successive additions to its several surfaces, and preserves its form, with a considerable addition to its magnitude. This curious fact was originally noticed by Le Blanc, who has founded on it a method of obtaining large and perfect crystals.

In some instances, the affinity of a salt for its solvent is so powerful, that it will not separate from it in the form of crystals; but will yet crystallize from another fluid, which is capable of dissolving it, and for which it has a weaker affinity. Pot-ash, for instance, cannot be made to crystallize from its watery solution, but will yet

separate, in a regular form, from its solution in alcohol.

Every solid, that is susceptible of crystallization, has a tendency to assume a peculiar shape. Thus, common salt, when most perfectly crystallized, forms regular cubes; nitre has the shape of a six-sided prism; and alum that of an octahedron. It has, indeed, been alleged, as an objection to the modern theory of crystallization, that minerals, differing essentially in their composition, have precisely the same primitive form. For example, the primitive form of carbonate of lime, and of the compound carbonate of lime and magnesia, is, in both, a regular rhomboid, so nearly resembling each other, as to have been supposed to be precisely the same. this case, however, Dr. Wollaston has shown, that though the figures are similar, yet their angles, on admeasurement by a nice instrument, differ very appreciably\*. But other instances have been since brought forward by M. Beudant, in which artificial salts, composed of dissimilar ingredients, have the same crystalline form; and Dr. Wollaston has satisfied himself of the accuracy of M. Beudant's remark, that the mixed sulphates of copper and iron, of zinc and iron, and of copper, zinc and iron, assume forms, in which no difference has yet been discovered from that of simple sulphate of iron alonet. He apprehends, indeed, that on minute investigation, some difference will be found, either in the angles or linear measures of those different salts; but till this has been established, the facts, as they stand, must be acknowledged to be exceptions to the principle, that identity of crystalline form is necessarily connected with identity of chemical composition. In the instances which have been given, the perfect transparency of the crystals forbids our considering them as an intermixture of foreign matter grouped together by sulphate of iron; and this explanation is, also, irreconcileable with the fact, discovered by Dr. Wollaston, that a mixed solution of sulphates of zinc and copper, in certain proportions, affords crystals which, though containing no iron, still agree so nearly in form with

<sup>\*</sup> Phil. Trans. 1812.

those of sulphate of iron that he could not undertake to point out

any difference between them.

It has been long known that the same solid admits of great varieties of crystalline figure, without any variation of its chemical composition. Calcareous spar, for example, appears in six-sided prisms, in three or six-sided pyramids, and in many other shapes. These varieties are occasioned by accidental circumstances, which modify the operation of the force of cohesion. The diversities of shape are, on first view, extremely numerous; and yet, upon a careful examination and comparison, they are found to be reducible to a small number of simple figures, which, for each individual species, is always the same.

The attempt to trace all the observed forms of crystals to a few simple or primary ones, seems to have originated with Bergman\*. In the instance of calcareous spar, this distinguished chemist demonstrated that its numerous modifications may possibly result from one simple figure, the rhomb, by the accumulation of which, in various ways, crystals of the most opposite forms may be generated. This theory he extended to crystals of every kind; and he accounted for the differences of their external figures, by varie-

ties of their mechanical elements or minute molecules.

About the same period with Bergman, or immediately afterwards, M. Romé de l'Isle pursued still farther the theory of the structure of crystals. He reduced the study of crystallography to principles more exact, and more consistent with observation. He classed together, as much as he was able, crystals of the same nature. among the different forms belonging to the same species, he selected, for the primitive form, one which appeared to him to be the most proper, on account of its simplicity. Supposing this to be truncated in different manners, he deduced the other forms, and established a certain gradation, or series of passages, from the primitive form to complicated figures, which on first view would scarcely appear to have any connexion with it. To the descriptions and figures of the primitive forms, he added the mechanical measurement of the principal angles, and showed that these angles are constantly the same in each variety. It must be acknowledged, however, that the primitive forms, assumed by this philosopher, were entirely imaginary, and not the result of any experimental analysis. His method was to frame an hypothesis; and then to examine its coincidence with actual appearances. On his principles any form might have been the primitive one, and any other have been deduced from it.

It was reserved for the sagacity of the Abbé Hauy to unfold the true theory of the structure of crystals, and to support it both by experimental and mathematical evidence. By the mechanical division of a complicated crystal, he first obtains the simple form, and afterwards constructs, by the varied accumulation of the primitive figure, according to mathematical synthesis, all the observed varie-

ties of that species.

<sup>\*</sup> Bergman's Essays, vol. ii.

Every crystal may be divided by means of proper instruments: and, if split in certain directions, presents plane and smooth surfaces. If split in other directions, the fracture is rugged, is the mere effect of violence, and is not guided by the natural joining of the crystal. This fact had been long known to jewellers and lapidaries; and an accidental observation of it proved, to the Abbé Hauy, the key of the whole theory of crystallization. By the skilful division of a six-sided prism of calcareous spar, he reduced it to a rhomb, precisely resembling that which is known under the name of Iceland crystal. Other forms of calcareous spar were subjected to the same operation; and, however different at the outset, finally agreed in yielding, as the last product, a rhomboidal solid. 'It was discovered also by Hauy, that if we take a crystal of another kind (the cubic fluor spar for instance,) the nucleus, obtained by its mechanical division, will have a different figure, viz. an octahedron. Other crystallized bodies produce still different forms; which are not, however, very nu-Those which have hitherto been discovered, are reducible to six; the parrallelopipedon, which includes the cube, the rhomb, and all the solids which are terminated by six faces, parallel two and two; the tetrahedron; the octahedron; the regular hexahedral prism; the dodecahedron with equal and similar rhomboidal planes;

and the dodecahedron with triangular planes.

The solid of the primitive form or nucleus of a chrystal, obtained by mechanical division, may be subdivided in a direction parallel to its different faces. All the sections thus produced being similar, the resulting solids are precisely similar in shape to the nucleus, and differ from it only in size, which continues to decrease as the division is carried farther. To this division, however, there must be a limit, beyond which we should come to particles so small, that they could no longer be divided. At this term, therefore, we must stop: and to these last particles, the result of an analysis of the primitive nucleus, and similar to it in shape, Hauy has given the name of the integrant molecule. If the division of the nucleus can be carried on in other directions than parallel to its faces, the integral molecule may then have a figure different from that of the nucleus. The forms, however, of the integrant molecule, which have hitherto been discovered, are only three; the tetrahedron, the simplest of pyramids; the triangular prism, the simplest of prisms; and the parallelopipedon, including the cube and rhomboid, the simplest of solids which have their faces parallel two and two. With respect to octahedral crystals, there is a difficulty, whether the octahedron, or tetrahedron, is to be adopted as the primitive form; and, whichsoever be chosen, since neither of them can fill space without leaving vacuities, it is not easy to conceive any arrangement, by which the particles will remain at rest. To obviate this difficulty, Dr. Wollaston has suggested that, in such instances, the elementary particles may be perfect spheres; and by the due application of spheres to each other, he has shown, that a variety of crystalline forms may be produced\*; viz. the octahedron, the tetrahedron, and the acute rhomboid. If other particles, having the same relative arrangement, be supposed to have the shape of oblate spheroids, the regular rhomboid will be the resulting figure; and if the spheroids be oblong instead of oblate, they will generate prisms of three or six sides. The cube, also, Dr. Wollaston has shown, may be explained by the aggrega-

tion of spheroidical particles.

A method of developing the structure of crystals, by a new process, which appears greatly superior to that of mechanical divisions, has been lately described by Mr. Danielt. It consists in exposing any moderately soluble salt to the slow and regulated action of a solvent. A shapeless mass of alum, for instance, weighing about 1500 grains, being immersed in 15 ounce measures of water, and set by, in a quiet place, for a period of three or four weeks, will be found to have been more dissolved toward the upper than the lower part, and to have assumed a pyramidal form. On further examination, the lower end of the mass will present the form of octahedrons and sections of octahedrons, in high relief and of various dimensions. They will be most distinct at its lower extremity, becoming less so as they ascend. This new process of dissection admits of extensive application. Borax, in the course of six weeks, exhibits eight sided prisms with various terminations; and other salts may be made to unfold their external structure by the slow agency of water. Carbonate of lime, carbonate of strontites, and carbonate of barytes. give also distinct results, when acted upon by weak acids; and even amorphous masses of those metals, which have a tendency to assume a crystalline form, such as bismuth, antimony, and nickel, when exposed to very dilute nitric acid, presented at the end of a few days distinct crystalline forms. The results of these experiments, when minutely traced and investigated, as has been ably done in Mr. Daniel's Memoir, afford strong confirmation to the theory, that the spheroidical is the true form of the ultimate particles of crystallized bodies.

The primitive form, and that of the integral molecule having been experimentally determined by the dissection of a crystal, the next step is to discover the law, according to which these molecules are arranged, in order to produce, by their accumulation around the primitive figure, the great variety of secondary forms. What is most important in the discoveries of Haüy, and what constitutes in fact the essence of his theory, is the determination of these laws, and the precise measurement of their action. He has shown that all the parts of a secondary crystal, superadded to the primitive nucleus, consist of laminæ, which decrease gradually by the subtraction of one or more layers of integrant molecules; so that theory is capable of determining the number of these ranges, and, by a necessary consequence, the exact form of the secondary crystal.

By the development of these laws of decrement, Hauy has shown

<sup>\*</sup> Phil. Trans. 1813, p. 51.

<sup>†</sup> Jour. of Science and the Arts, i. 24.

how, from variations of the arrangement of the integrant molecules, a great variety of secondary figures may be produced. Their explanation, however, would involve a minuteness of detail, altogether unsuitable to the purpose of this work; and I refer therefore, for a very perspicuous statement of them, to the first and ninth volumes of the Philosophical Magazine.

## SECTION II.

Of Chemical Affinity, and the General Phenomena of Chemical Action.

CHEMICAL affinity, like the cohesive attraction, is effective only at insensible distances; but it is distinguished from the latter force, in being exerted between the particles or atoms of bodies of different kinds. The result of its action is not a mere aggregate, having the same properties as the separate parts, and differing only by its greater quantity or mass, but a new compound, in which the properties of the components have either entirely or partly disappeared, and in which new qualities are also apparent. The combinations effected by chemical affinity are permanent, and are destroyed only by the interference of a more powerful force, either of the same or of a different kind.

As a general exemplification of chemical action, we may assume that which takes place between potash and sulphuric acid. In their separate state, each of these bodies is distinguished by striking peculiarities of taste, and by other qualities. The alkali, on being added to blue vegetable infusions, changes their colour to green; and the acid turns them red. But if we add the one substance to the other, very cautiously and in small quantities, examining the effect of each addition, we shall at length attain a certain point, at which the liquid will possess neither acid nor alkaline qualities; the taste will be converted into a bitter one; and the mixture will produce no effect on blue vegetable colours. Here then, the qualities of the constituent parts, or at least some of their most important ones, are destroyed by combination. When opposing properties thus disappear, the bodies combined have been said to saturate each other; and the precise term, at which this takes place, has been called the point of saturation. It is adviseable, however, to restrict this expression to weaker combinations, where there is no remarkable alteration of qualities, as in cases of solution: and to apply to those results of more energetic affinities, which are attended with loss of properties, the term *neutralization*.

At the same time that the properties of bodies disappear on combination, other new qualities, both sensible and chemical, are acquired; and the affinities of the components for other substances become in some cases increased, in others, diminished in energy. Sulphur, for example, is destitute of taste, smell, or action on vegetable

colours; and oxygen gas is, in these respects, equally inefficient. But the compound of sulphur and oxygen is intensely acid; the minutest portion instantly reddens blue vegetable infusions; and the acid is disposed to enter into combination with a variety of bodies, for which its components evinced no affinity. Facts of this kind sufficiently refute the opinion of the older chemists, that the properties of compounds are intermediate between those of their component parts; for in instances like the foregoing the compound has qualities, not a vestige of which can be traced to either of its elements.

It is not, however, in all cases, that the change of properties is so distinct and appreciable by the senses, as in the instances which have been just now described. In some examples of chemical union, the change is scarcely perceptible to the eye or taste, when the chemist is nevertheless certain that combination must have taken place. This occurs chiefly in the mixture of saline solutions with each other, where a complete exchange of principles ensues, without any evident change of properties. Examples of this kind cannot, however, be understood, till the subject of complex affinity has been first elucidated.

The existence of chemical affinity between any two bodies is inferred, therefore, from their entering into chemical combination; and that this has happened, a change of properties may be considered as a sufficient proof, even though the change may not be very obvious, and may require accurate examination to be perceived

The proof, which establishes the nature of chemical compounds, is of two kinds, synthesis and analysis. Synthesis consists in effecting the chemical union of two or more bodies; and analysis in separating them from each other, and exhibiting them in a separate When we have a compound of two or more ingredients, which are themselves compounded also, the separation of the compounds from each other may be called the proximate analysis of the body; and the farther separation of these compounds into their most simple principles, its ultimate analysis. Thus the proximate analysis of sulphate of potash consists in resolving it into potash and sulphuric acid; and its ultimate analysis is effected by decomposing the potash into potassium and oxygen, and the sulphuric acid into oxygen and sulphur.

When the analysis of any substance has been carried as far as possible, we arrive at its most simple principles, or elements, by which expression we are to understand, not a body that is incapable of further decomposition, but only one which has not yet been decomposed. The progress of chemical science, for several centuries past, has consisted in carrying still farther the analysis of bodies, and in proving those to be compounded, which had before

been considered as elementary.

Beside the alteration of properties, which usually accompanies chemical action, there are certain other phenomena, which are generally observed to attend it.

1st. In almost every instance of chemical union, the specific gra-

vity of the compound is greater than might have been inferred from that of its components; and this is true both of weaker and more energetic combinations. When equal weights of water and sulphuric acid are made to combine, the specific gravity of the resulting liquid is not the mean, but considerably greater than the mean. The law extends also to solids. But though general, it is not universal; for in a very few instances, chiefly of aëriform fluids, condensation does not attend chemical union. And in the combination of metals with each other the reverse even takes place, the compound being specifically lighter than might have been expected, from the specific gravity of its elements, and their proportion to each other.

2dly. When bodies combine chemically, it may be received as a general fact, that their temperature changes. Equal weights of oil of vitriol and water, both at the temperature of 50° of Faht, are heated, by sudden mixture, to considerably above 212°. In other examples, a contrary effect takes place, and a diminished temperature, or, in other words, a production of cold, is observed. This is all that it is at present necessary to state on the subject, which will

be more fully considered when we come to treat of caloric.

Sdly. The forms of bodies are often materially changed by chemical combination. Two solids may, by their union, become fluid; or two fluids may become solid. Solids are also often changed into aëriform fluids; and, in many instances, the union of two airs, or gases, is attended with their sudden conversion into the solid state. By long exposure of quicksilver to a moderate heat, we change it from a brilliant liquid into a reddish scaly solid; and by heating this solid in a retort, we obtain an aëriformifluid, or gas, in considerable quantity, and recover the quicksilver in its original form.

4thly. Change of colour is a frequent, but not universal concomitant of chemical action. In some cases, brilliant colours are destroyed, as when oxymuriatic acid is made to act on solution of indigo. In other instances, two substances, which are nearly colourless, form, by their union, a compound distinguished by beauty of colour, as when liquid potash is added to a very dilute syrup of violets. Certain colours appear also to belong essentially to chemical compounds, and to be characteristic of them. Thus 100 parts of quick-silver, and 4 of oxygen, invariably give a black compound; and the same quantity, with 8 parts of oxygen, a red compound.

#### SECTION III.

Of the Proportions in which bodies combine; and of the Atomië Theory.

In the chemical combination of bodies with each other, a few leading circumstances deserve to be remarked.

1st. Some bodies unite in all proportions; for example, water and

sulphuric acid, or water and alcohol.

2dly. Other bodies combine in all proportions, as far as a certain point, beyond which, combination no longer takes place. Thus water will take up successive portions of common salt, until at length it becomes incapable of dissolving any more. In cases of this sort, as well as in those included under the first head, combination is weak and easily destroyed, and the qualities which belonged to the components in their separate state continue to be apparent in the compound.

3dly. There are many examples in which bodies unite in one proportion only; and in all such cases the proportion of the elements of a compound must be uniform for the species. Thus hydrogen and oxygen unite in no other proportions, than those constituting water, which, by weight, are very nearly 11½ of the former to 88½ of the latter, or 1 to 7½. In cases of this sort, the combination is generally energetic; and the characteristic qualities of the compo-

nents are no longer observable in the compound.

4thly. Other bodies unite in several proportions: but these proportions are definite, and, in the intermediate ones, no combination ensues. Thus 100 parts by weight of charcoal combine with 1324 of oxygen, or with 265, but with no intermediate quantity; 100 parts of manganese combine with 14 of oxygen, or with 28, or with

42, or with 56, and with those proportions only.

Now it is remarkable, that when one body enters into combination with another, in several different proportions, the numbers indicating the greater proportions are exact simple multiples of that denoting the smallest proportion. In other words, if the smallest proportion in which B combines with A, be denoted by 10, A may combine with twice 10 of B, or with three times 10, and so on; but with no intermediate quantities. There cannot be a more striking instance of this law than that above mentioned, of the compounds of manganese with oxygen; in which the oxygen of the three last compounds may be observed to be a multiplication of that of the first (14), by the numbers 2, 3, and 4. Examples, indeed, of this kind have, of late, so much increased in number, that the law of simple multiples bids fair to become universal, with respect at least to chemical compounds, the proportions of which are definite.

Facts of this kind are not only important in themselves, but also on account of the generalizations that have been deduced from them; for on them Mr. Dalton has founded what may be termed the Atomic Theory of the chemical Constitution of Bodies. Till this theory was proposed, we had no adequate explanation of the uniformity of the proportions of chemical compounds; or of the nature of the cause which renders combination, in other proportions, impossible. In this place I shall offer only a brief illustration of the theory; for in the course of the work I shall have occasion to apply

it to the explanation of a variety of phenomena.

Though we appear, when we effect the chemical union of bodies, to operate on masses, yet it is consistent with the most rational

view of the constitution of bodies to believe, that it is only between their ultimate particles, or atoms, that combination takes place. By the term atoms, it has been already stated, we are to understand the smallest parts of which bodies are composed. An atom, therefore, must be mechanically indivisible, and of course a fraction of an atom cannot exist. Whether the atoms of different bodies be of the same size, or of different sizes, we have no sufficient evidence. The probability is, that the atoms of different bodies are of unequal sizes; but it cannot be determined whether their sizes bear any regular proportion to their weights. We are equally ignorant of their shape; but it is probable, though not essential to the theory, that they are spherical. This, however, requires a little qualification. The atoms of all bodies probably consist of a solid corpuscle, forming a nucleus, and of an atmosphere of heat, by which that corpuscle is surrounded; for absolute contact is never supposed to take place between the atoms of bodies. The figure of a simple atom may readily, therefore, be conceived to be spherical. But in compound atoms, consisting of a single central atom, surrounded by other atoms of a different kind, it is obvious that the figure (contemplating the solid corpuscles only) cannot be spherical; yet if we include the atmosphere of heat, the figure of a compound atom may be spherical, or some shape approaching to a sphere.

Taking for granted that combination takes place between the atoms of bodies only, Mr. Dalton has deduced, from the relative weights in which bodies unite, the relative weights of their ultimate particles, or atoms. When only one combination of any two elementary bodies exists, he assumes, unless the contrary can be proved, that its elements are united atom to atom singly. Combinations of this sort he calls binary. But if several compounds can be obtained from the same elements, they combine, he supposes, in proportions expressed by some simple multiple of the number of atoms. The following table exhibits a view of some of these combinations:

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1 atom of A + 1 atom of B = 1 atom of C, binary.
1 atom of A + 2 atoms of B = 1 atom of D, ternary.
2 atoms of A + 1 atom of B = 1 atom of E, ternary.
1 atom of A + 3 atoms of B = 1 atom of E, quaternary.
3 atoms of A + 1 atom of B = 1 atom of E, quaternary.
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A different classification of atoms has been proposed by Berzelius, viz. into, 1stly, 'elementary atoms; 2ndly, compound atoms. The compound atoms he divides again into three different species, namely, 1st, atoms formed of only two elementary substances united, or compound atoms of the first order: 2dly, atoms composed of more than two elementary substances; and these, as they are only found in organic bodies, or bodies obtained by the destruction of organic matter, he calls organic atoms: 3dly, atoms formed by the union of two or more compound atoms; as for example, the salts. These he calls compound atoms of the second order.

If elementary atoms of different kinds were of the same size, the

greatest number of the atoms of A that could be combined with an atom of B would be 12; for this is the greatest number of spherical bodies that can be arranged in contact with a sphere of the same diameter. But this equality of size, though adopted by Berzelius, is not necessary to the hypothesis of Mr. Dalton; and is indeed, sup-

posed by him not to exist.

As an illustration of the mode in which the weight of the atoms of bodies is determined, let us suppose that any two elementary substances, A and B, form a binary compound; and that they have proved experimentally to unite in the proportion, by weight, of 5 of the former to 4 of the latter; then since according to the hypothesis, they unite particle to particle, those numbers will express the relative weights of their atoms. But besides combining atom to atom singly, 1 atom of A may combine with 2 of B, or with 3, 4, &c. Or 1 atom of B may unite with 2 of A, or with 3, 4, &c. When such a series of compounds exists, the relative proportion of their elements ought necessarily, on analysis, to be proved to be 5 of A to 4 of B; or 5 to (4+4=) 8; or 5 to (4+4+4=) 12, &c.; or, contrariwise, 4 of B to 5 of A; or 4 to (5 + 5 =) 10; or 4 to (5 +5 + 5 =) 15. Between these there ought to be no intermediate compounds; and the existence of any such (as 5 of A to 6 of B, or 4. of B to 72 of A) would, if clearly established, militate against the hypothesis.

To verify these numbers, it may be proper to examine the combinations of A and B with some third substance, for example, with C. Let us suppose that A and C form a binary compound, in which analysis discovers 5 parts of A and 3 of C. Then, if C and B are, also, capable of forming a binary compound, the relative proportion of its elements ought to be 4 of B to 3 of C; for these numbers denote the relative weights of their atoms. Now this is precisely the method, by which Mr. Dalton has deduced the relative weights of oxygen, hydrogen, and nitrogen; the two first from the known composition of water, and the two last from the proportion of the elements of ammonia. Extending the comparison to a variety of other bodies, he has obtained a scale of the relative weights of their atoms.

In several instances, additional evidence is acquired of the accuracy of the weight, assigned to an element, by our obtaining the same number from the investigation of several of its compounds.

For example:

In water, the hydrogen is to the oxygen as
 In olefiant gas, the hydrogen is to the carbon as
 In carbonic oxide the oxygen is to the carbon as
 to 5.65.
 to 5.65.

Whether, therefore, we determine the weight of the atom of carbon, from the proportion in which it combines with hydrogen, or with oxygen, we arrive at the same number 5.65; an agreement which as it occurs in various other instances, can scarcely be an accidental coincidence. In a similar manner, 7.5 is deducible, as representing the atom of oxygen, both from the combination of that Vol. I—G

base with hydrogen and with carbon; and 1 is inferred to be the relative weight of the atom of hydrogen from the two principal com-

pounds into which it enters.

In selecting the body, which should be assumed as unity, Mr. Dalton has been induced to fix on hydrogen, because it is that body which unites with others in the smallest proportion. Thus, in water, we have 1 of hydrogen by weight to 7½ of oxygen in ammonia, 1 of hydrogen to 5 of nitrogen; in carburetted hydrogen, 1 of hydrogen to 5 of carbon; and in sulphureted hydrogen, 1 of hydrogen, to 15 of sulphur. Taking for granted that all these bodies are binary compounds, we have the following scale of numbers, expressive of the relative weights of the atoms of their elements:

Hydrogen	•		•	•		•	1
Oxygen .							
Nitrogen							5.05
Carbon .							
Sulphur .							

Drs. Wollaston and Thomson, and Professor Berzelius, on the other hand, have assumed oxygen as the decimal unit, chiefly with a view to facilitate the estimation of its numerous compounds with other bodies. This, perhaps, is to be regretted, even though the change may be in some respects eligible, because it is extremely desirable that chemical writers should employ an universal standard of comparison for the weights of the atoms of bodies. It is easy, however, to reduce their numbers to Mr. Dalton's by the rule of proportion. Thus as 10 (the number of Drs. Wollaston and Thomson for oxygen) is to 1.32 (their number of hydrogen) so very nearly is 7.5 (Mr. Dalton's number for oxygen) to 1 (his number for hy-

drogen)

Sir H. Davy has assumed, with Mr. Dalton, the atom of hydrogen as unity; but that philosopher, and Berzelius also, have modified the theory, by taking for granted that water is a compound of one proportion (atom) of oxygen, and two proportions (atoms) of hydrogen. This is founded on the fact, that two measures of hydrogen gas and one of oxygen gas, are necessary to form water; and on the supposition, that equal measures of different gases contain equal numbers of atoms. And as, in water, the hydrogen is to the oxygen by weight as 1 to 7.5, two atoms or volumes of hydrogen must, on this hypothesis, weigh 1, and one atom or volume of oxygen 7.5, or if we denote a single atom of hydrogen by 1, we must express an atom of oxygen by 15. It is objectionable, however, to this modification of the atomic theory, that it contradicts a fundamental proposition of Mr. Dalton, the consistency of which with mechanical principles he has fully shown; namely, that when one combination only of two elements exists, as between oxygen and hydrogen, it must be presumed, unless the contrary can be proved, to be a binary one.

It is easy to determine, in the manner already explained, the relative weights of the atoms of two elementary bodies, which unite only in one proportion. But when one body unites, in different proportions, with another, it is necessary, in order to ascertain the weight of its atom, that we should know the smallest proportion in which the former combines with the latter. Thus, if we have a body A, 100 parts of which by weight combine with not less than 30 of oxygen, the relative weight of its atom will be to that of oxygen as 100 to 30; or, reducing these numbers to their lowest terms, as 25 to 7.5; and the number 25 will, therefore, express the relative weight of the atom of A. But if, in the progress of science, it should be found, that 100 parts of A are capable of uniting with 15 parts of oxygen, then the relative weight of the atom of A must be doubled, for, as 100 is to 15, so is 50 to 7.5. This example will serve to explain the changes, that have been sometimes made, in assigning the weights of the atoms of certain bodies; changes, which, it may be observed, always consist either in a multiplication, or division, of the original weight, by some simple number.

There are (it must be acknowledged) a few cases, in which one body combines with another in different proportions; and yet the greater proportions are not multiples of the less, by any entire number. For example, we have two oxides of iron, the first of which consists of 100 iron and about 30 oxygen; the second of 100 iron and about 45 oxygen. But the numbers 30 and 45 are to each other as 1 to 1½. It will, however, render these numbers (1 and 1½) consistent with the law of simple multiples, if we multiply each of them by 2, which will change them to 2 and 3; and if we suppose that there is an oxide of iron (though it has not yet been obtained experimentally), consisting of 100 iron and 15 oxygen; for the multiplication of this last number by 2 and 3, will then give us the known

oxides of iron.

In some cases, where we have the apparent anomaly of 1 atom of one substance, united with 1½ of another, it has been proposed, by Dr. Thomson\*, to remove the difficulty, by multiplying both numbers by 2; and by assuming that, in such compounds, we have 2 atoms of the one combined wish 3 atoms of the other. Such combinations, it is true, are exceptions to a law deduced by Berzelius; that, in all inorganic compounds, one of the constituents is in the state of a single atom. But they are in no respect inconsistent with the views of Mr. Dalton; and are, indeed, expressly admitted by him to be compatible with his hypothesis, as well as confirmed by experiencet. Thus it will appear, in the sequel, that some of the compounds of nitrogen with oxygen are constituted in this way.

Several objections have been proposed to the theory of Mr. Dal-

ton; but, of these, I shall notice only the most important.

1. It has been contended, that we have no evidence, when one combination only of two elements exists, that it must be a binary one; and that we might equally well suppose it to be a compound of two atoms of the one body, with one atom of the other. In answer to this objection, we may urge the probability that when two elementary bodies A and B unite, the most energetic combination will

<sup>\*</sup> Thomson's Annals, v. 187.

<sup>†</sup> Thomson's Annals, iii. 174.

be that in which one atom of A is combined with one atom of B; for an additional atom of B will introduce a new force, diminishing the attraction of those elements for each other, namely, the mutual repulsion of the atoms of B; and this repulsion will be the greater, in proportion as we increase the number of the atoms of B.

2dly. It has been said, that, when more than one compound of two elements exist, we have no proof which of them is the binary compound, and which the ternary; for example, that we might suppose carbonic acid to be a compound of an atom of charcoal and an atom of oxygen, and carbonic oxide to be a compound of an atom of oxygen with two atoms of charcoal. To this objection, however, it is a satisfactory answer, that such a constitution of carbonic acid and carbonic oxide would be directly contradictory of a law of chemical combination, namely, that it is attended, in most cases, with an increase of specific gravity. It would be absurd, therefore, to suppose carbonic acid, which is the heavier body, to be only once compounded, and carbonic oxide, which is the lighter, to be twice compounded. Moreover, it is universally observed, that of chemical compounds, the most simple are the most difficult to be decomposed; and this being the case with carbonic oxide, we may naturally suppose it to be more simple than carbonic acid.

Sdly. It has been remarked, that instead of supposing water to consist of an atom of oxygen united with an atom of hydrogen, and that the atom of the former is 7½ times heavier than that of the latter, we might, with equal probability, conclude that, in water, we have 7½ times more atoms, in number, of oxygen than of hydrogen. But this, if admitted, would involve the absurdity, that in a mixture of hydrogen and oxygen gases, so contrived that the ultimate atoms of each should be in equal number, seven atoms of oxygen should desert all the proximate atoms of hydrogen, in order to unite with one at a distance, for which they must necessarily have a less affinity. In this case, a less force must overcome a greater; and, finally, only a small number of the atoms of hydrogen would be engaged by the atoms of oxygen, the rest remaining in a state of freedom.

It would be claiming too much, however, for the theory of Mr. Dalton, to assert that, in its present state, it is to be considered as fully established in all its details. In the further progress of chemical discovery, it is probable that it will receive considerable modifications, and that the relative weights of the atoms of bodies will, in many cases, be essentially changed. The instances, in which the theory agrees with the result of analysis, are already too numerous to allow them to be considered as accidental coincidences; and no phenomena have hitherto been shown to be irreconcileable with the hypothesis. Its value and importance, if confirmed by the accession of new facts, will be scarcely less felt as a guide to further investigations into the constitution of bodies, than as a test of the accuracy of our present knowledge; and the universality of its application to chemical phenomena will be scarcely inferior to

that of the law of gravitation in explaining the facts of natural phi-

losophy\*.

A modification of the law of definite proportions, so far as respects aëriform bodies,, has been proposed by Gay Lussac, namely, that they combine in proportions determinable not by weight but by volume, the ratios being 1 measure of A to 1 of B, or 1 to 2, or 1 to Water, for example, results from the union of 2 volumes of hydrogen with 1 volume of oxygen; muriate of ammonia from 1 volume of muriatic acid gas + 1 of ammonia; nitrous gas from 1 measure of oxygen + 1 of nitrogen; nitrous oxide from 1 oxygen + 2 nitrogen; nitrous acid from 2 oxygen + 1 nitrogen. In some instances, as in that of water, this law is not inconsistent with the atomic theory; but in other instances it cannot be reconciled with the relative weights assigned to the atoms of certain elementary bo-In nitrous gas, for example, which Mr. Dalton conceives to be formed by the union of 1 atom of oxygen + 1 atom of nitrogen, equal volumes of those gases would give for the relative weights of oxygen and nitrogen, numbers differing widely from those derived by other methods. The two hypotheses of atoms and of volumes cannot, therefore, both be true; and from some well ascertained exceptions to the latter, it appears to me that the theory of volumes will scarcely be found tenable.

Before dismissing the consideration of the proportions in which bodies combine, it will be proper to notice a few general principles, which, though they are connected with the atomic theory, have been

derived from experience.

1. When we have ascertained the proportion in which any two or more bodies A B C &c. of one class neutralize another body X of a different class, it will be found that the same relative proportions of A B C &c. will be required to neutralize any other body of the same class as X. Thus, since 100 parts of real sulphuric acid, and 68 (omitting fractions) of muriatic acid neutralize 118 of potash, and since 100 of sulphuric acid neutralize 71 of lime, we may infer that 68 of muriatic acid will neutralize the same quantity (71) of lime. The great importance of this law will readily be perceived, not only as it enables us to anticipate, but also to correct, the results of analysis.

2dly. If the quantities of two bodies, A and B, that are necessary to saturate a given weight of a third body X, be represented by q and r, these quantities may be called equivalents. Thus, in the example above cited, 100 parts of sulphuric acid and 68 of muriatic acid, are equivalents of each other. A Table of Equivalents, which will be found extremely useful in various calculations, will be given in the Appendix. By adapting a table of this sort to a moveable scale, on the principle of Gunter's sliding rule, Dr. Wollaston has lately constructed an instrument, called the Logometric Scale of

<sup>\*</sup> A perspicuous and able statement of the atomic theory, published by Mr. Ewart, in the sixth volume of Thomson's Annals, deserves the reader's perusal.

Chemical Equivalents, which is capable of solving, with great facility, a number of problems, interesting both to the scientific and practical chemist\*.

#### SECTION IV.

# Of Elective Affinity.

An important law of affinity, which is the basis of almost all chemical theory, is, that one body has not the same force of affinity towards a number of others, but attracts them unequally. will combine with B in preference to C, even when these two bodies are presented to it under equally favourable circumstances. Or, when A is united with C, the application of B will detach A from C, and we shall have a new compound consisting of A and B, C being set at liberty. Such cases are examples of what is termed in chemistry simple decomposition, by which it is to be understood that a body acts upon a compound of two ingredients, and unites with one of its constituents, leaving the other at liberty. And as the forces of affinity of one body to a number of others vary, this body has been metaphorically represented as making an election; and the affinity has been called single elective affinity. Thus, if to the muriate of lime, consisting of lime and muriatic acid, we add potash, the muriatic acid exerts a stronger elective affinity for the potash than for the lime; and the lime falls down in the state of a powder, or is precipitated. Of facts of this kind a great variety have been comprehended in the form of tables, the first idea of which seems to have occurred nearly a century ago, to Geoffroy, a French chemist. substance, whose affinities are to be expressed, is placed at the head of a column, and is separated from the rest by a horizontal line. Beneath this line are arranged the bodies, with which it is capable of combining, in the order of their respective forces of affinity; the substance which it attracts most strongly being placed nearest to it, and that, for which it has the least affinity, at the bottom of the column. The affinities of muriatic acid, for example, are exhibited by the following plan:-

MURIATIC ACID.

Barytes, Potash, Soda, Lime, Ammonia, Magnesia, &c. &c.

This instrument may be had, with printed instructions for its use, of Mr. Carey, 182, Strand, London; and its cost is so trifling, that I consider a plate of it to be quite unnecessary.

Simple decomposition may be expressed also by another form, contrived by Bergman. Thus, the following scheme illustrates the decomposition of muriate of magnesia by potash:—

Muriate of Potash.

Muriate of Muriatic acid. Potash. Water at 60°.

Magnesia. Magnesia.

The original compound (muriate of magnesia) is placed on the outside and to the left of the vertical bracket. The included space contains the original principles of the compound, and also the body which is added to produce decomposition. Above and below the horizontal lines are placed the results of their action. The point of the lower horizontal line being turned downwards, denotes that the magnesia falls down or is precipitated; and the upper line, being perfectly straight, shows, that the muriate of potash remains in solution. If both the bodies had remained in solution, they would both have been placed above the upper line; or, if both had been precipitated, beneath the lower one. If either one or both had escaped in a volatile form, this would have been expressed by placing the volatilized substance above the diagram, and turning upwards the middle of the upper horizontal line. But since decompositions vary under different circumstances, it is necessary to denote, by the proper addition to the scheme, that the bodies are dissolved in water of the temperature of 60°.

No chemical facts can appear, on first view, more simple or intelligible, than those which are explained by the operation of single elective affinity. It will be found, however, on a more minute examination, that this force, abstractedly considered, is only one of several causes which are concerned in chemical decompositions, and that its action is modified, and sometimes even subverted, by conn-

teracting forces.

## SECTION V.

Of the Causes which modify the Action of Chemical Affinity.

THE order of decomposition is not, as might be inferred from the law of elective affinity, invariable; but, in certain cases, may even be reversed. Thus though A may attract B more strongly than either A or B is attracted by C, yet, under some circumstances, C may be employed to decompose partially the compound A B. Again, if we mix together A B and C, using the two first in the proportions required to neutralize each other, it will be found that A

and B have not combined to the exclusion of C, but that we have a compound of B with A, and another of B with C, in proportions regulated by the quantities of A and C, which have been employed. Facts of this kind have been long known to chemists. It had been ascertained, for example, before the time of Bergman, that sulphate of potash, a salt composed of sulphuric acid and potash, is partly decompounded by nitric acid, although the nitric has a weaker affinity than the sulphuric acid for that alkali. Examples of the same kind have since been multiplied by Berthollet, who has asserted that in the following, as well as in other cases, a substance possessing a weaker attraction, displaces another having a stronger, for a third body\*:

- 1. Potash separates sulphuric acid from barytes.
- 2. Lime separates sulphuric acid from potash.
- 3. Potash separates oxalic acid from lime.
- 4. Nitric acid separates lime from oxalic acid.
- 5. Potash separates phosphoric acid from lime.
- 6. Potash separates carbonic acid from lime.
- 7. Soda separates sulphuric acid from potash.

These facts, and a variety of similar ones, are to be explained, according to the views of Berthollet, on the following principles:

1. When two substances are opposed to each other with respect. to a third, as in the foregoing examples, they may be considered as antagonist forces; and they share the third body between them in proportion to the intensity of their action. But this intensity, according to Berthollet, depends not only on the energy of the affinities, but on the quantities of the two bodies opposed to each other. Hence a large quantity of one of the substances may compensate a weaker affinity, and the reverse. To the absolute weight of a body, multiplied by the degree of its affinity, he has given the name of mass, a term in some degree objectionable from the different meaning which is affixed to it in mechanical philosophy. As an illustration, let us suppose (what is not accurate in point of fact) that the affinity of barytes for muriatic acid is twice as strong as that of potash, or that these affinities are respectively denoted by the numbers 4 and 2. In this case, the same mass will result from 4 parts of barytes as from 8 of potash; because the same product (16) is obtained in each instance, by multiplying the number indicating the affinity into that denoting the quantity; for 4 (the affinity of barytes) multiplied by 4, (the quantity assumed in this example) is equal to 16; and 2 (the affinity of potash) multiplied by 8 (its quantity) is also equal to 16. In this case, therefore, to divide equally a portion of muriatic acid between barytes and potash, these bodies

In each of the examples given in the Table, the body, first mentioned, decomposes a compound of the second and third, although its attraction for the second is inferior to that of the third.

should be employed in the proportion of 2 of the former to 4 of the latter.

The influence of quantity explains also the difficulty which is observed in effecting, in any instance, the total decomposition of a compound of two principles by means of a third. The immediate effect of a third body C, when added to a compound A B, is to abstract from B a portion of the substance A; and consequently a portion of B is set at liberty, the attraction of which for A is opposed to that of the uncombined part of C. The farther this decomposition is carried, the greater will be the proportion of B, will it oppose any farther tendency of C to detach the substance A. At a certain point, the affinities of B and C for A will be exactly balanced, and the decomposition will proceed no farther. In a few cases, it is acknowledged by Berthollet, a third body separates the whole of one of the principles of a compound; but this he supposes to happen in consequence of the agency of other extraneous forces, the nature of which remains to be pointed out.

2dly. Cohesion is a force, the influence of which over the chemical union of bodies has already been explained in a former section; and other illustrations of its interference will be given, when we con-

sider the subject of the limitations to chemical combination.

Sdly. Insolubility is another force, which essentially modifies the exertion of affinity. It is to be considered, indeed, merely as the result of cohesion, with respect to the liquid in which the effect

takes place.

When a soluble substance and an insoluble one are presented, at the same time, to a third, for which they have nearly an equal affinity, the soluble body is brought into the sphere of action with great advantages over its antagonist. Its cohesion at the outset is but little, and by solution is reduced almost to nothing; while that of the insoluble body remains the same. The whole of the soluble substance also exerts its affinity at once; while a part only of the insoluble one can oppose its force. Hence the soluble substance may prevail, and may attach to itself the greatest proportion of the third body, even though it has a weaker affinity than the insoluble one to the subject of combination.

Insolubility, however, under certain circumstances, is a force which turns the balance in favour of the affinity of one body when opposed to the affinity of another. For example, if to the soluble compound, sulphate of soda, we add barytes, the new compound, sulphate of barytes, is precipitated the instant it is formed: and being removed from the sphere of action the soda can exert no effect upon it by its greater quantity or mass. For the same reason when soda is added to sulphate of barytes, the sulphate is protected from decom-

position both by its insolubility and by its cohesion.

These facts sufficiently prove that the order of precipitation, which was formerly assumed as the basis of tables of elective affinity, can no longer be considered as an accurate measure of that force; and that the body, which is precipitated, may in some cases, be superior

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in affinity to the one which has caused precipitation. In these cases, a trifling superiority in affinity may be more than counter-balanced

by the cohesive force, which causes insolubility.

4thly. Great specific gravity is a force, which must concur with insolubility or cohesion in originally impeding combination; and when chemical union has taken place, it must come in aid of affinity, by removing the new compound from the sphere of action. It is scarcely necessary to enlarge on the operation of a force, the nature of which must be so obvious.

5thly. Elasticity. Cohesion, it has already been stated, may prove an impediment to combination; and on the other hand it is possible that the particles of bodies may be separated so widely, as to be removed out of the sphere of their mutual attraction. Such appears to be the fact with regard to a class of bodies called airs or gases. The bases of several of these have powerful attractions for the bases of others, and for various liquids, and yet they do not combine on simple admixture, but strong mechanical pressure brings their particles sufficiently near, to be within the influence of their mutual attraction,

and combination immediately ensues.

Again, if two bodies, one of which has an elastic and the other a liquid form, be presented at the same time to a solid, for which they have both an affinity, the solid will unite with the liquid in preference to the gas. Or if we add to the compound of an elastic substance with an inelastic one, a third body also inelastic, the two latter combine to the exclusion of the elastic body. For example, if to the compound of potash and carbonic acid we add sulphuric acid, the latter acid, acting both by its affinity and its quantity, disengages a portion of carbonic acid. This, by its elasticy, is removed from the sphere of action, and presents no obstacle to the farther operation of the sulphuric acid. Hence, elastic bodies act only by their affinity; whereas liquids act both by their affinity and quantity conjoined. And though the affinity of the liquid, abstractedly considered, may be inferior to the affinity of the elastic body, yet, united with quantity, it In the above instances, the whole of the elastic acid may be expelled by the fixed acid; whereas it has already been observed, decomposition is incomplete, if the substance which is liberated remain within the sphere of action.

6thly. Efflorescence is a circumstance which occasionally influences the exertion of affinity; but this is only a very rare occurrence. The simplest example of it is that of lime, and muriate of soda. When a paste composed of these two substances with a great excess of lime, is exposed, in a moist state, to the air, the lime, acting by its quantity, disengages soda from the common salt which appears in a dry form, on the outer surface of the paste, united with carbonic acid absorbed from the atmosphere. In this case, the soda, which is separated, being removed from contiguity with the interior part of the mass, presents no obstacle to the farther action of the lime, and the decomposition is carried farther than it would have been, had no such

removal happened.

7thly. The influence of temperature over chemical affinity is ex-

tremely extensive and important; but at present a very general statement only of its effects is required. In some cases an increased temperature acts in promoting, and at others in impeding, chemical combination: and it materially affects also the order of decompositions.

An increased temperature promotes chemical union by diminishing or overcoming cohesion. Thus metals unite by fusion, and several salts are more soluble in hot than in cold water. Whenever heat is an obstacle to combination, it produces its effect by increasing elasticity. Hence water absorbs a less proportion of gas at a high than at a low temperature. A reduction of the temperature of elastic bodies, by lessening their elasticity, facilitates their union with other substances. In certain cases, an increased temperature has the combined effects of diminishing cohesion and increasing elasticity. When sulphur is exposed to oxygen gas, no combination ensues, until the sulphur is heated; and though the elasticity of the gas is thus increased, yet the diminution of cohesion of the solid is more than proportionate, and chemical union ensues between the two bodies.

8thly. The electrical state of bodies has a most important influence over their chemical union. This, however, is a subject, of which it would be difficult to offer a general view, and for its full development, I refer to a subsequent chapter on Electro-che-

mistry.

9thly. Mechanical pressure is another force, which has considerable influence over chemical affinity. With respect to solid bodies, its agency is not frequent; but we have unequivocal examples of its operation in cases, where detonation is produced by concussion. The effects of pressure are chiefly manifested, in producing the combination of aëriform bodies either with solids, with liquids, or with each other; and in preserving combinations, which have been already formed, under circumstances tending to disunite them. Chalk, for example, is a compound of lime and carbonic acid; and these bodies, by the simple application of an intense heat, are separable from each other; but, under strong pressure, a heat may be applied sufficient to melt the chalk, without expelling the carbonic acid. It is this principle, (of the influence of pressure in opposing chemical decomposition,) that is the foundation of Dr. Hutton's ingenious Theory of the Earth.

Such are the most important circumstances, that modify the exertion of chemical affinity. Of their influence, sufficient illustrations have been given to prove, that in every case of combination and decomposition, we are not to consider the force of affinity abstractedly; but are to take into account the agency of other powers, as cohesion, quantity, insolubility, elasticity, efflorescence, and temperature. By the action of these extraneous powers, Berthollet has endeavoured to explain certain facts which are not easily understood on any other principle. Of these, the most important are, 1stly, the establishment of proportions in chemical compounds; and 2dly, the modification produced in the affinities of bodies by chemical union.

1. Independently of these extraneous forces, Berthollet imagines that there are no limits to combination, or that two bodies, which are now susceptible of union only in one or in few proportions, might, if these forces were annihilated, be united in every proportion. The causes which he has assigned, as chiefly regulating proportion, are cohesion and elasticity. To take one of the simplest cases, the proportion, in which a salt can be combined with water, depends on the balance between the chemical affinity of the bodies for each other, and the cohesive attraction of the salt. In this case, then, cohesion is the limiting power. As an example of the influence of this force when more energetic affinities are exerted, if we add to diluted sulphuric acid a solution of barytes, a compound is formed, consisting of sulphuric acid and barytes, which in consequence of its great insolubility or cohesion, is instantly removed from contact with the redundant acid, and with established proportions.

The agency of elasticity in limiting proportion, may be exemplified by the combination of hydrogen and oxygen. If a mixture of the two gases be inflamed, the new compound, water, is immediately separated, from what is superfluous of both ingredients, by its superior density. In other instances, the bases of aëriform substances are combined in various proportions, and in such examples, there are several terms of greatest condensation, as in the

case of oxygen and nitrogen.

2. Another important part of the theory of Berthollet is, that the affinities of a compound are not newly acquired; but are merely the modified affinities of its constituents, the action of which, in their separate state, was counteracted by the prevalence of opposing forces. By combination, these forces are so far overcome, that the af-

finities of the constituents are enabled to exert themselves.

The action of different affinities existing in one compound, Berthollet terms resulting affinities, while the individual affinities of the constituents he calls elementary affinities. Thus nitric acid acts on potash, by an affinity, which results from those of oxygen and azote for potash. And as all affinity is mutual, the term resulting affinity is applied, also, to that force, with which a simple body acts on a compound; to the affinity for example, which any simple body may exert on nitric acid. A simple body, indeed, may exert towards a compound both an elementary and resulting affinity. If the elementary affinity prevails, it will unite only with one of the principles of the compound, as when a simple body, by its affinity for oxygen, decomposes nitric acid, and liberates its nitrogen in a separate form. If the resulting affinity be predominant, the simple body will unite with the whole compound without effecting any disunion of its elements.

From these views it may be inferred, that we are not, in any case, to deny the existence of an affinity between two bodies, merely because they do not combine when presented to each other; for an affinity may exist, but may be suppressed by the prevalence of opposing forces. According to the doctrine of Berthollet, affinity is a force exerted by every body towards every other; even though not made apparent by any effect. On this principle, we are able to ex-

plain certain phenomena, which are wholly unintelligible on any other, and especially those which have been referred to disposing affinity. The action of sulphuret of potash, for example, on oxygen gas, has been ascribed to the disposing affinity of potash for sulphuric acid. This, however, is ascribing an affinity to a compound, before that compound has existence. It is much more probable, that besides the diminishing cohesion of the sulphur, the affinity of potash for oxygen has some share in producing the combination. On this principle the united affinities of the potash and sulphur for oxygen (in other words the resulting affinities of the sulphuret of potash) are the efficient causes of chemical union. This explanation, at least, does not, like the theory of disposing affinities, involve an absurdity.

The theory of Berthollet, however, which promised, on its first development, to form a new era in chemical philosophy, has lost much of its probability, by the subsequent progress of the science. It is directly, indeed, at variance with the doctrine of definite proportions, which every day gathers strength by the accumulation of new and well established facts. It is liable, moreover, to the fol-

lowing objections.

1st. It has been shown by Professor Pfaff, of Kiell\*, that, in various cases, where two acids are brought into contact with one base, the base unites with one acid, to the entire exclusion of the other. When, for example, to a given weight of lime, quantities of sulphuric and tartaric acids are put, either of which would exactly saturate the lime, the sulphuric acid unites with the lime, to the entire exclusion of the tartaric. The same evidence of a superior affinity of the sulphuric acid over that of the oxalic is obtained, by placing those acids in contact with as much oxide of lead, as would exactly saturate either of them. Again, comparing the action of two bases on one acid, the same law is found to hold good: for when potash and magnesia are mixed with just as much sulphuric acid, as is required to saturate either of them, the potash seizes the whole of the acid, and no part of it unites with the magnesia. Nor can these effects be explained by any of those extraneous forces, which Berthollet supposes, in all cases, to regulate chemical combination; or by any principle, but a stronger affinity of sulphuric acid, than of tartaric or oxalic acid, for the different bases; and of potash, than of magnesia, for the same acid.

2dly. Some of the cases, before quoted from Berthollet, to show the reciprocal displacement of two bodies by each other from a third (it has been justly observed), are examples, not of single elective affinity, in which three bodies only are concerned; but of complex affinity, in which the attractions of four bodies are brought into action. In the first case, for example, there is reason to believe, that sulphuric acid is displaced from barytes, not by pure potash, but by potash which has absorbed carbonic acid from the atmosphere.

3dly. In other cases, the consideration of the affinities of two bodies A and B, for a third C, is complicated with this circum-

<sup>\* 77</sup> Ann. de Chim. p. 259.

stance, that the neutral compound of A and B has an affinity for a farther portion of one of its ingredients. If then C be brought into contact with the compound A B, we have, acting at the same moment, the affinity of C for A, which partly decomposes the compound A B; and the affinity of the undecomposed part of A B, for that portion of B which is set at liberty. For instance, when nitric acid acts on sulphate of potash, some nitrate of potash is formed; and the sulphuric acid, which is set at liberty, uniting with the undecomposed sulphate of potash, composes a new salt, consisting of sulphate of potash with an excess of sulphuric acid.

4thly. It is a strong objection to the theory of Berthollet that, in some cases, decompositions happen, which, according to his views, onght not to take place; and that in others, decompositions do not ensue, which the theory would have led us to have anticipated.

5thly. The theory is objectionable, inasmuch as, in several instances, properties are supposed to operate, before the bodies exist, to which those properties are attributed. It is inconceivable, for instance, that the cohesion, or insolubility of sulphate of barytes, can have any share in producing the decomposition of sulphate of potash by that earth; for the insolubility of sulphate of barytes can have no agency, till that compound is formed; which is the very effect to be explained.

Notwithstanding these objections to the theory of Berthollet, when carried so far as has been done by its author, in the explanation of chemical phenomena, it must still be admitted that the extraneous forces, pointed out by that acute philosopher, have great influence in modifying the effects of chemical affinity. But these forces are entitled only to be considered as secondary causes; and not as determining combinations or decompositions, nor as regulating the proportions in which bodies unite, independently of the superior force of chemical affinity.

### SECTION VI.

# Of the Estimation of the Forces of Affinity.

The affinities of one body for a number of others are not all of the same degree of force. This is all that the present state of our knowledge authorises us to affirm; for we are ignorant how much the affinity of one body for another is superior to that of a third. The determination of the precise forces of affinity would be an important step in chemical philosophy: for its phenomena would then be reduced to calculation; and we should be enabled to anticipate the results of experiment. That the force of chemical affinity must be prodigiously great, is evident from its effect in preserving the combination of water with some bodies (the alkalies for instance) when exposed to a violent heat; notwithstanding its great expansive force, and though water is not essential to the constitution of those bodies.

The observed order of decomposition, it has already been stated, does not enable us to assign the order of the forces of affinity; because, in all decompositions, other forces are concerned. We are, therefore, obliged to seek some other method of determining the

problem. Of these, several have been proposed.

When the surface of one body is brought into contact with another surface of the same kind, as when the smooth surfaces of a divided leaden bullet are pressed together, they adhere by the force of cohesion, their particles being all of the same kind. But when the surfaces of different bodies are thus brought into apparent contact, it is reasonable to suppose that their adhesion arises from chemical affinity, because their particles are of different kinds. Guyton proposed, therefore, the comparative force, with which different surfaces adhere, as a competent measure of chemical affinity. His experiments were made on plates of different metals, of precisely the same size and form, suspended by their centres from the arm of a sensible balance. The lower surfaces of these plates were successively brought into contact with mercury, which was changed for each experiment, and the weight was observed, which it was necessary to add to the opposite scale, in order to detach the several metals. Those which required the largest weight were inferred to have the greatest affinity; and it is remarkable that the order of affinities, as determined in this way, correspond with the affinities as ascertained by other methods. The following were the results:

Gold adhered to mercury with a force of								446 grains.		
Silver	-	-		- '	-	· _	-	429		
Tin	-	_ `	-	-	-	-	-	418		
Lead	-		-	-	-	-	-	397		
Bismuth	-	-	-	_	-	-	-	372		
Zinc	-	-	-	-	-	-	-	204		
Copper	-	-	-	-	-	-	-	142		
Copper Antimony	r	-	-	-	-	-	-	126		
Iron	-	-	-	-	-	• •	-	115		
Cobalt	-	<b>-</b> '	-	-	-	-	Ĺ	8		

This method, it must be obvious, is of too limited application to be of much utility; for few bodies have the mechanical conditions, which can enable us to subject them to such a test. How, for example, could the affinities of acids for alkalies be examined on this principle? It may be doubted, also, whether in the cases to which it may be applied, it does not measure the facility of combination, rather than the actual force of affinity.

To determine the absolute forces of affinity, which one body exerts towards a number of others, Mr. Kirwan has proposed the quantity of each which is required to produce neutralization, in other words, its equivalent. This he has ascertained by experiment in a great variety of instances, a few of which are contained in the following tables; the numbers being altered, to accommodate them to

recent discoveries.

# 100 Parts of BULPHURIC ACID require for Neutralization

194 parts of barytes.
138 . . . of strontites.
118 . . . of potash.

78.2 . . of soda.

71 . . . of lime. 49.2 . . of magnesia. 43 . . . of amonia. 100 Parts of POTASH require

115 of nitric acid
93 of carbonic acid.
84.5 of sulphuric.
58 of muriatic.

In judging of the affinities of the same acid for different bases. Mr. Kirwan assumed that they are represented by the numbers indicating the quantities of each base required for neutralization, Thus, because 100 parts of sulphuric acid neutralize 194 of barytes, and 118 of potash, the affinity of the former is superior to that of the latter in the proportion of 194 to 118. So far the inference corresponds with the order of decomposition; for barytes takes sulphuric acid from potash. But if we examine the affinities of potash. as represented in the second table, we shall find that, on this principle, they are directly contradictory to fact. Thus the affinity of sulphuric acid should be inferior to that of the carbonic; whereas it is well known that the former displaces the latter from all its combinations. Mr. Kirwan was, therefore, driven to the necessity of establishing a precisely opposite rule in determining the affinities of different acids for the same base, and of assuming that they are inversely proportionate to the affinity of the saturating acid. the affinity of carbonic acid for potash would be represented by 84.5, and that of sulphuric acid 93. This, however, involves a contradiction; since it is implied that a stronger affinity, in one instance, requires a greater quantity of the saturating principle, as in the relation of barytes and potash to sulphuric acid; and that, in the other, it requires a less quantity, as in the instance of the sulphuric and carbonic acids with respect to potash.

Since neutralization is an effect of chemical affinity, which must in all cases bear a proportion to its cause, it has been assumed by Berthollet, that the substance which, in the smallest quantity, neutralizes another, is the one possessing the strongest affinity. On this principle the affinities of sulphuric acid for different bases, will be exactly the reverse of the order established by Mr. Kirwan; and to that order, which would have been assigned from observed decompositions. Thus ammonia will have a stronger affinity for sulphuric acid, than any of the substances which are placed above in the table; though it is separated, by each of these, from its union

with that acid.

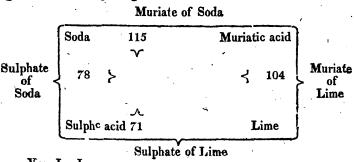
It is in the extraneous forces, which have been enumerated as influencing chemical affinity, that we are to seek, according to Berthollet, for the explanation of this apparent anomaly, and especially in the forces of cohesion and elasticity. The elasticity of ammonia, for example, turns the balance in favour of magnesia, lime, &c.

There is an obvious difficulty, however, in the application of the theory. For as the elasticity of ammonia is suppressed by its combination with sulphuric acid, what, it may be asked, but a superior affinity for sulphuric acid, existing in the substances which stand above ammonia in the table, can occasion the first commencement of decomposition? The problem, therefore, of determining the absolute forces of affinity can scarcely be admitted to be solved. Even if it were, we should not be able to predict the order of decomposition, unless the modifying forces of cohesion, elasticity, &cc. could be at the same time subjected to precise admeasurement. Until both these objects are accomplished, the results of chemistry can in no case be obtained by calculation, but the science must remain a collection of general principles, derived from experiment and induction.

## SECTION VII.

# Of Complex Affinity.

UNDER the more general name of complex affinity, Berthollet includes that which has hitherto been considered as produced by the action of four affinities, and which has commonly been denominated double elective affinity. It frequently happens that the compound of two principles cannot be destroyed either by a third or a fourth separately applied; but if the third and fourth be combined, and placed in contact with the former compound, a decomposition or a change of principles will ensue. Thus when lime water is added to a solution of the sulphate of soda, no decomposition happens, because the sulphuric acid attracts soda more strongly than it attracts lime. If the muriatic acid be applied to the same compound, still its principles remain undisturbed, because the sulphuric acid attracts soda more strongly than the muriatic. But if the lime and muriatic acid, previously combined, be mixed with the sulphate of soda, a double decomposition is effected. The lime, quitting the muriatic acid, unites with the sulphuric; and the soda, being separated from the sulphuric acid, combines with the muriatic. These decompositions are rendered more intelligible by the following diagram, contrived by Bergman.



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On the outside of the vertical brackets are placed the original compounds; and above and below the diagram, the new compounds. The upper line, being straight, indicates that the muriate of soda remains in solution; and the middle of the lower line, being directed

downwards, that the sulphate of lime is precipitated.

In all cases similar to the foregoing, Mr Kirwan conceives that we may trace the operation of two distinct series of affinities. The affinities tending to preserve the original compounds (which in the above example are those between sulphuric acid and soda, and between muriatic acid and lime), he terms the quiescent affinities; because they resist any change of composition. On the other hand, the affinities, which tend to disunite the original compounds and to produce new ones (such as those between muriatic acid and soda, and between sulphuric acid and lime), he terms divellent affinities. In order that an effect may be produced, the divellent affinities must necessarily be superior to the quiescent. Now assuming the numbers in Mr. Kirwan's tables to express accurately the forces of affinities, the double exchange of principles, which happens in the preceding instance, is readily explained. Thus the quiescent affinities are

Those of lime to muriatic acid=104
of soda to sulphuric acid= 78

The divellent affinities, opposed to these consist of

The affinity of soda to muriatic acid = 115

lime to sulphuric acid = 71

182

The original compound, therefore, is preserved by a force equivalent to 182, and the tendencies to produce new compounds are represented by the number 186. The divellent affinities are, therefore,

predominant.

The theory of quiescent and divellent affinities, however, though highly attractive from its simplicity, and from the facility with which it solves certain phenomena, is completely defective in the explanation of others. For example, sulphate of potash is decomposed by muriate of barytes. Yet, estimating in the above manner the quiescent and divellent affinities, an exchange of principles ought not to ensue. The affinities tending to preserve the original compound, are those of sulphuric acid for potash=118, and of muriatic acid for barytes=285. The divellent affinities are that of muriatic acid for potash=174 + that of sulphuric acid for barytes=194. The quiescent affinities then are 118 + 285 = 403, and the divellent 174 + 194 = 368. This leaves a balance of 35 in favour of the quiescent affinities; and yet decomposition ensues, when the two compounds are brought into contact.

It must be acknowledged that the numbers, assumed by Mr. Kirwan, do not correspond with the actual forces of affinity. But even if they are taken according to the principle assumed by Berthollet, they will not be found universally applicable. The reason of this is, that the phenomena produced by complex affinity, like those occasioned by simple affinity, are materially influenced by the extraneous forces of cohesion, quantity, elasticity, temperature, &c. The effect of quantity is shown by the fact, that if two salts be mixed together in certain proportions, decomposition will ensue, but not if mixed in other proportions. Thus from the mingled solutions of two parts of muriate of lime and one of nitrate of potash, we obtain muriate of potash; but not from equal weights of the two salts. Insolubility, or precipitation, has also a considerable influence on the When this occurs, the influence of quantity is destroyed, as in the case of sulphate of potash and muriate of barytes. Elasticity, and an increased temperature (which operates by increasing elasticity), and the reverse of this, or a greatly diminished temperature, have also a powerful influence in promoting the action of complex affinities. Thus of four principles, two of which are of complex affinities. volatile and two fixed, the two of which are volatile will be disposed to unite, in preference to combining with either of those which are fixed. The nature of the fluid, in which salts are dissolved, has also an important influence on their tendency to mutual decomposition\*. Thus changes take place in the midst of an alcoholic medium, which do not happen to the same bodies dissolved in watert. We have even instances, in which though a compound A B decomposes another compound C D, A uniting with C, and B with D, yet (which could not have been expected à priori) the compound A C is reciprocally decomposed by D B, and the original compounds A B and C D are regenerated. Hence the phenomena of complex decomposition concur with those of a more simple kind, in proving that affinity is not an uniform force, but is materially influenced by various modifying circumstances; and that we cannot confidently anticipate results, from comparing the numerical expressions of quiescent and divellent affinities.

One great obstacle to the construction of tables, capable of representing the forces of affinity, is the difficulty of ascertaining, with precision, the quantities of bodies required for neutralization. Notwithstanding all the care employed by Mr. Kirwan, considerable errors appear to have crept into the results of his experiments. This will sufficiently appear, when they are examined by a test, originally proposed by Guyton. It must be obvious that if between two salts, which are mixed together in solution, decomposition should ensue, and the mixture should afterwards be found neutral, the quantity of acid, which has quitted one of the bases, must have been exactly equivalent to the saturation of the other base, also deserted by its acid. If, for example, we mingle the muriate of magnesia and sulphate of soda, the mixture continues neutral; and hence it fol-

<sup>\*</sup> Ann. de Chim. et Phys. iv. 366.

See the sect. on Sulphate of Barytes.

<sup>†</sup> Dr. Murray on Sea Water.

lows that the muriatic acid, which has quitted the magnesia, must have been exactly equal to the neutralization of the soda, deserted by the sulphuric acid. But from a calculation, founded on the proportion of the ingredients of these salts, as established by Mr. Kirwan, it appears that the soda, detached from the sulphuric acid, is not adequate to the saturation of the muriatic acid. The mixture, therefore, ought to be acid; and since this is contrary to fact, we may safely infer that there is an error in the estimation of the ingredients composing these salts. No tables, indeed, can be correct, unless they stand the test of this mode of verification. Such a table has been calculated by Fischer from the experiments of Richter; but even this table seems in several respects to be of questionable accuracy. I have thought it, however, entitled to a place among the tables in the Appendix; and I shall annex, also, a more correct one, the data of which are chiefly supplied by Dr. Wollaston's paper on Chemical Equivalents\*.

# SECTION VIII.

Experimental Illustrations of Chemical Affinity, Solution, &c.

For these experiments, a few wine glasses, or, in preference, deep ale glasses, will be required; and a Florence flask for performing the solutions.

I. Some bodies have no affinity for each other.—Oil and water, mercury and water, or powdered chalk and water, when shaken together in a vial, do not combine, the oil or water always rising to the surface, and the mercury or chalk sinking to the bottom.

II. Examples of chemical affinity, and its most simple effect, viz. solution.—Sugar or common salt disappears or dissolves in water; chalk in dilute muriatic acid. Sugar and salt are, therefore, said to be soluble in water, and chalk in muriatic acid. The liquid in which the solid disappears is termed a solvent or menstruum. Chalk or sand, on the contrary, when mixed with water by agitation, always subsides again. Hence they are said to be insoluble.

III. Influence of mechanical division in promoting the action of chemical affinity, or in favouring solution.—Lumps of chalk or marble dissolve much more slowly in dilute muriatic acid, than equal weights of the same bodies in powder. Muriate of lime, or nitrate of ammonia, cast, after liquefaction by heat, into the shape of a solid sphere, is very slowly dissolved; but with great rapidity what in the state of a powder or of crystals. When a lump of the Derbythire fluate of lime is immersed in concentrated sulphuric acid, scalled any action of the two substances on each other takes

<sup>\*</sup> Phil. Trans. 1814.

<sup>†</sup> I omit, purposely, the distinction between the solution and dissolution.

place; but if the stone be finely pulverized, and then mingled with the acid, a violent action is manifested, by the copious escape of vapours of fluoric acid. In the common arts of life, the rasping and grinding of wood and other substances are familiar examples.

IV. Hot liquids, generally speaking, are more powerful solvents than cold ones.—To four ounce-measures of water, at the temperature of the atmosphere, add three ounces of sulphate of soda in powder. Only part of the salt will be dissolved, even after being agitated some time. Apply heat, and the whole of the salt will disappear. When the liquor cools, a portion of salt will separate again in a regular form or in crystals. This last appearance affords an in-

stance of crystalization.

To this law, however, there are several exceptions; for many salts, among which is muriate of soda, or common salt, are equally, or nearly equally, soluble in cold as in hot water. (See the table of solubility of salts in water, in the Appendix.) Hence, a hot, and saturated solution of muriate of soda does not, like the sulphate, deposit crystals on cooling. To obtain crystals of the muriate, and of the other salts which observe a similar law as to solubility, it is necessary to evaporate a portion of the water; and the salt will then be deposited, even while the liquor remains hot. In general, the more slow the cooling, or evaporation, of saline solutions, the larger and more regular are the crystals.

V. A very minute division of bodies is effected by solution.—Dissolve two grains of sulphate of iron in a quart of water, and add a few drops of this solution to a wine-glassfull of water, into which a few drops of tincture of galls have been fallen. The dilute infusion of galls will speedily assume a purplish hue. This shows that every drop of the quart of water, in which the sulphate of iron was

dissolved, contains a notable portion of the salt.

VI. Some bodies dissolve much more readily and copiously than others.—Thus, an ounce measure of distilled water will dissolve half its weight of sulphate of ammonia, one third its weight of sulphate of soda, one sixteenth of sulphate of potash, and only one

five-hundredth its weight of sulphate of lime.

VII. Mechanical agitation facilitates solution.—Into a wineglassfull of water, tinged blue with the infusion of litmus, let fall a small lump of solid tartaric acid. The acid, if left at rest, even during some hours, will only change to red that portion of the infusion which is in immediate contract with it. Stir the liquor, and

the whole will immediately become red.

VIII. Bodies do not act on each other, unless either one or both be in a state of solution, or at least contain water.—1. Mix some dry tartaric acid with dry bi-carbonate of soda, and grind them together in a mortar. No combination will ensue till water is added, which, acting the part of a solvent, promotes the union of the acid and alkali, as appears from a violent effervescence. It has been shown by Link\*, that the water of crystallization, existing in certain salts, acts

<sup>\*</sup> Thomson's Annals, vii. 426,

as free water in occasioning chemical action. For example, acetate of lead and sulphate of copper, both in crystals, become green when triturated together, a proof of the mutual decomposition of those two salts.

2. Spread thinly, on a piece of tinfoil, three or four inches square, some dry nitrate of copper\*, and wrap it up. No effect will follow. Unfold the tinfoil, and having sprinkled the nitrate of copper with the smallest possible quantity of water, wrap the tinfoil up again as quickly as possible, pressing down the edge closely. Considerable heat, attended with fumes, will now be excited; and, if the experiment has been dexterously managed, even light will be evolved. This shows that nitrate of copper has no action on tin, unless in a state of solution.

IX. Bodies, even when in a state of solution, do not act on each other at perceptible distances; in other words, contiguity is essential to the action of chemical affinity.—Thus, when two fluids of different specific gravities, and which have a strong affinity for each other, are separated by a thin stratum of a third, which exerts no remarkable action on either, no combination ensues between the uppermost and lowest stratum. Into a glass jar, or deep ale glass, pour two ouncemeasures of a solution of subcarbonate of potash, containing, in that quantity, two drachms of common salt of tartar. Under this, introduce, very carefully, half an ounce-measure of water, holding in solution a drachm of common salt; and again, under both these, two ounce-measures of sulphuric acid, which has been diluted with an equal weight of water, and allowed to become cool. The introduction of a second and third liquid beneath the first, is best effected, by filling, with the liquid to be introduced, the dropping tube, fig. 15. pl. i. which may be done by the action of the mouth. ger is then pressed on the upper orifice of the tube; and the lower orifice, being brought to the bottom of the vessel containing the liquid, the finger is withdrawn, and the liquid descends from the tube, without mingling with the upper stratum. When a solution of carbonate of potash is thus separated from diluted sulphuric acid, for which it has a powerful affinity, by the intervention of a thin stratum of brine, the two fluids will remain distinct and inefficient on each other; but on stirring the mixture, a violent effervescence ensues, in consequence of the action of the sulphuric acid on the potash.

X. Two bodies, having no affinity for each other, unite by the intervention of a third.—Thus, the oil and water which, in Experiment I., could not, by agitation, be brought into union, unite immediately on adding a solution of caustic potash. The alkali, in this case, acts as an intermedium. The fact, indeed, admits of being explained by the supposition, that the oil and alkali form in the first instance, a compound which is soluble in water.

XI. Saturation and neutralization illustrated.—Water, after having taken up as much common salt as it can dissolve, is said to

<sup>\*</sup> To prepare nitrate of copper, dissolve the filings or turnings of that metal in a mixture of one part nitrous acid and three parts water; decant the liquor when it has ceased to emit fumes; and evaporate it to dryness, in a copper or earthen dish. The dry mass must be kept in a bottle:

be saturated with salt. Muriatic acid, when it has ceased to act any

longer on lime, is said to be neutralized, as is also the lime.

XII. The properties characterizing bodies, when separate, are destroyed by chemical combination, and new properties appear in the compound.—Thus, muriatic acid and lime, which, in a separate state, have each a most corrosive taste, lose this entirely when mutually saturated; the compound is extremely soluble, though lime itself is very difficult of solution; the acid no longer reddens syrup of violets; nor does the lime change it, as before, to green. The resulting compound, also, muriate of lime, exhibits new properties. It has an intensely bitter taste; is susceptible of a crystallized form; and the crystals, when mixed with snow or ice, generate a degree of cold sufficient to freeze quicksilver.

XIII. Single elective affinity illustrated.—1. Add to the combination of oil with alkali, formed in Experiment X., a little diluted sulphuric acid. The acid will seize the alkali, and set the oil at liberty, which will rise to the top. In this instance, the affinity of alkali for acid is greater than that of alkali for oil. 2. To a dilute solution of muriate of lime (prepared in Experiment II.), add a little of the solution of pure potash. The potash will seize the muri-

atic acid, and the lime will fall down, or be precipitated.

XIV. In every instance, in comparing the affinities of two bodies for a third, a weaker affinity, in one of the two compared, will be found to be compensated by increasing its quantity.—It is not easy to offer clear and unequivocal examples of this law, and such as the student may submit to the test of experiment. The following, however, may illustrate the proposition sufficiently: Mingle together, in a mortar, one part of muriate of soda (common salt) with half a part of red oxide of lead (litharge, or red lead), and add sufficient water to form a thin paste. The oxide of lead, on examining the mixture after twenty-four hours, will be found not to have detached the muriatic acid from the soda; for the strong taste of that alkali will not be apparent. Increase the weight of the oxide of lead to three or four times that of the salt; and, after the same interval, the mixture will exhibit, by its taste, marks of uncombined soda. This proves, that the larger quantity of the oxide must have detached a considerable portion of muriatic acid from the soda, though the oxide has a weaker affinity for that acid than the soda possesses.

Another illustration of the same general principle has been suggested by Berzelius. It is necessary to premise, that the colour of the compound of sulphuric acid with oxide of copper is blue, and that of muriatic acid with the same oxide, green. To a saturated solution of sulphate of copper in water, add by degrees concentrated muriatic acid. Every addition will render the colour of the liquid more distinctly green, showing an increased production of muriate of copper; the oxide of copper being divided between the sulphuric and muriatic acids, in proportion to the quantity of each

acid that is present.

XV. Double elective affinity exemplified.—In a watery solution of sulphate of zinc, immerse a thin sheet of lead: the lead will re-

main unaltered, as also will the sulphate of zinc, because zinc attracts sulphuric acid more strongly than lead. But let a solution of acetate of lead be mixed with one of sulphate of zinc; the lead will then go over to the sulphuric acid, while the zinc passes to the acetic. The sulphate of lead being insoluble, will fall down in the state of a white powder; but the acetate of zinc will remain in solution. The changes that occur in this experiment will be better understood from the following scheme:

# Sulphate of Zinc Water at 60° Sulpha Acetate Of Lead Sulphate of Lead.

The vertical brackets include the original compounds, viz. sulphate of zinc, and acetate of lead; and the horizontal line and bracket point out the new ones, viz. acetate of zinc and sulphate of lead. By the upper horizontal line, it is denoted, that the acetate of zinc remains in solution; and, by the point of the lower bracket being directed downwards, it is meant to express, that the sulphate of lead falls down, or is precipitated.

# CHAPTER III.

OF HEAT OR CALORICA

### SECTION I.

# General Observations on Heat.

WHEN we apply the hand to a body which is hotter than itself, we are sensible of a peculiar feeling, which we agree to call the sensation of heat. At the same time we observe, in almost all bodies that are placed in the same situation with the hand, certain effects, the most remarkable of which is an enlargement of their dimensions. These circumstances with very few exceptions, so constantly ac-

company each other, that we can have little or no hesitation in referring them to one and the same cause. Of the nature of this cause we have no satisfactory evidence; and we are unable to demonstrate either that it consists in any general quality of bodies, or that it resides in a distinct and peculiar kind of matter. The opinion, however, which best explains the phenomena, is that which ascribes them to an extremely subtile fluid, of so refined a nature, as to be capable of insinuating itself between the particles of the most dense and solid bodies. To this fluid, as well as to the sensation which it excites, the term heat was formerly applied. But there was an obvious impropriety in confounding, under one appellation, two things so distinct as a sensation and its cause; and the term caloric, first proposed by Lavoisier, is now, therefore, generally adopted to denote the cause of heat. Occasionally, however, in order to avoid too frequent a repetition of the same word, the term heat is still employed in a more extensive sense, to express not only the sensation which it usually denotes, but also some of the modifications of caloric.

Caloric, so far as its chemical agencies are concerned, may be chiefly considered under two views—as an antagonist to the cohesive attraction of bodies—and as concurring with, and increasing elasticity. By removing the particles of any solid to a greater distance from each other, their cohesive attraction is diminished; and one of the principal impediments to their union with other bodies is overcome. On the other hand, caloric may be infused into bodies in such quantity, as not only to overcome cohesion, but to place their particles beyond the sphere of chemical affinity. Thus, in the class of substances, called gases, the ponderable ingredient, whether solid or liquid, is dissolved in so much caloric, that in mechanical properties the gases agree with the air of our atmosphere, especially in being permanently elastic. Different bodies of this class do not, in general, unite by simple mixture. But if, of two gases, we employ either one or both in a state of great condensation, or compress their particles nearer to each other by any means, the gravitating matter of both unites, and forms a new compound. Thus hydrogen and oxygen gases remain together in a state of mixture, for any length of time, without combining; but if we force their particles into a state of contiguity, by sudden and violent mechanical pressure, they unite and compose water. In many cases, also when two bodies are combined together, one of which is fixed, and the other becomes elastic by union with caloric, we are able, by its interposition alone, to effect their disunion. Thus carbonate of lime gives up its carbonic acid by the mere application of heat.

We may consider, then, all bodies in nature as subject to the action of two opposite forces, the mutual attraction of their particles on the one hand, and the repulsive power of caloric on the other; and bodies exist in the solid, liquid, or elastic state, as one or the other of these forces prevails. Water, by losing caloric, has its cohesion so much increased, that it assumes the solid form of ice; adding caloric, we diminish again its cohesion, and render it fluid; and,

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finally, by a still farther addition of caloric, we change it into vapour, and give it so much elasticity, that it may be rendered capable of bursting the strongest vessels. In many liquids, the tendency to elasticity is even so great, that they pass to the gaseous form by the

mere ranoval of the weight of the atmosphere.

Caloric, like all other bodies, may exist in two different states, in a state of freedom, and in a state, either of combination or of something nearly resembling it. In the former state, it is capable of exciting the sensation of heat, and of producing expansion in other bodies. To this modification the terms free or uncombined caloric, or caloric of temperature, have been applied. By the term temperature we are to understand the state of a body relatively to its power of exciting the sensation of heat, and occasioning expansion; effects which, in all probability, bear a proportion to the quantity of free caloric in a given space, or in a given quantity of matter. Thus what we call a high temperature may be ascribed to the presence of a large quantity of free caloric; and a low temperature to that of a small quantity. We are unacquainted, however, with the extremes of temperature; and may compare it to a chain, of which a few of the middle links only are exposed to our observation.

The degree of expansion produced by caloric, it will afterwards appear, bears a sufficient proportion to its quantity, to afford us a means of ascertaining the latter with tolerable accuracy. In estimating temperature, indeed, our senses are extremely imperfect: for we compare our sensations of heat, not with any fixed or uniform standard, but with those sensations, of which we have had immediately previous experience. The same portion of water will feel warm to a hand removed from contact with snow, and cold to another hand, which has been heated before the fire. To convey, therefore, any precise notion of temperature, we are obliged to describe the degree of expansion produced in some one body, which has been previously agreed upon as a standard of comparison. The standard most commonly employed is a quantity of quicksilver, contained in a glass ball, which terminates in a long narrow tube. This instrument, called a thermometer, is of the most important use in acquiring and recording our knowledge of the properties and laws of caloric. The thermometer, however, it must be obvious, is no otherwise a measure of the quantity of caloric, than as it ascertains the amount of one of its principal effects. In this respect, it stands in much the same predicament as the hygrometer, when considered as a mean of determining the moisture of the atmosphere. This last instrument, it may be remembered, is composed of some substance (such as a hair or a piece of whip-cord) which is lengthened by a moist atmosphere and contracted by a dry one; and in a degree proportionate to the moisture or dryness. But all the information, which the hygrometer gives us, is the degree of moisture between certain points that form the extremities of its scale; and it is quite incompetent to measure the absolute quantity of watery vapour in the air.

In explaining those properties and laws of caloric, which have become known to us by means of the thermometer, it appears a sufficiently natural division of the subject to describe, 1stly, those effects which caloric produces, without losing its properties of exciting the sensation of heat and occasioning expansion:—and, 2dly, those agencies, in which its characteristic properties are destroyed, and in which it ceases to be cognizable by our senses or by the thermometer.

The EXPANSION OF DILATATION of bodies, it will appear, is almost an universal effect of an increase of temperature. Its amount, however, is not the same in all bodies, but differs very essentially. By the same increase of temperature, liquids expand more than solids, and aëriform bodies more than either. Nor is the same quantity of expansion effected in the same solid or liquid, by adding similar quantities of heat; for, generally speaking, bodies expand by equal increments of caloric, more in high than in low temperatures. The explanation of this fact is, that the force opposing expansion (viz. cohesion) is diminished by the interposition of caloric between the particles of bodies: and, therefore, when equal quantities of caloric are added in succession, the last portions meet with less resistance to their expansive force than the first. In gases, which are destitute of cohesion, equal increments of heat appear, on the contrary, to be attended with precisely equal augmentations of bulk.

An important property of free caloric, the knowledge of which has been acquired by means of the thermometer, is its tendency to an equilibrium. When a heated ball of iron is exposed to the open air, the caloric, which is accumulated in it, flows out; and its temperature is gradually reduced to that of the surrounding medium. This is owing to two distinct causes: the air, immediately surrounding the ball, acquires part of the caloric which escapes; and, having its bulk increased, is rendered specifically lighter and ascends. This is succeeded by a cooler and heavier portion of air from above, which, in its turn, is expanded and carries off a second quantity of caloric. Hence a considerable part of the caloric, which is lost by a heated body, is conveyed away by the ambient air. But the refrigeration cannot be wholly explained on this principle; for it has been long known that heated bodies cool, though with less celerity, under the exhausted receiver of an air pump, and even in a Torricellian vacuum.

When the phenomena accompanying the cooling of bodies are accurately examined, it is found that a part of the caloric, which escapes, moves through the atmosphere with immeasurable velocity. In an experiment of M. Pictet, no perceptible interval took place between the time at which caloric quitted a heated body, and its reception by a thermometer at the distance of sixty-nine feet. It appears also to move with equal ease in all directions, and not to be at all impeded by a strong current of air meeting it transversely. Hence it follows that the propagation of caloric, in this state of rapid movement, does not depend on any agency of the medium through which it passes; a conclusion strengthened by the experiments of

Sir H. Davy, who has shown that, in a receiver exhausted to  $\frac{1}{20}$ , the effect of radiation is three times greater than in an atmosphere of the ordinary density. Like light, heat appears to be transmitted in parallel rays; and it has, therefore, under this modification, been called RADIANT CALORIC.

The proportion of caloric, lost by a heated body, in these two different ways, may be approximated by observing what time it takes to cool, through the same number of degrees, in air and in vacuo. By experiments of this kind, Dr. Franklin thought he had ascertained that a body, which requires five minutes in vacuo, will cool in air, through the same number of degrees, in two minutes. Count Rumford's experiments with a Torricellian vacuum give the proportions of 5 to 3. It will, perhaps, not be very remote from the truth, if it be stated, in general terms, that one half of the caloric, lost by a heated body, escapes by radiation, and that the rest is carried off by the ambient atmosphere.

The radiation of caloric appears to bear a proportion to the elevation of temperature of a body above that of the surrounding medium. Hence in part it is, that a heated body, during refrigeration, loses unequal quantities of caloric in equal times. The series appears to be pretty nearly a geometrical one. Thus, supposing the temperature of a body to be 1000 degrees above the surrounding medium,

This law of refrigeration, it is asserted by Dr. Delaroche, though nearly accurate at low temperatures, is far from being so at high ones.

The movement of caloric by radiation occurs only in free space, or through transparent media. But caloric is capable, also of passing through dense and opaque bodies, though with prodigiously impaired velocity. Thus a long bar of iron, heated at one end, requires considerable time to become hot at the other. This property in bodies has been called their conducting power, and it exists in different bodies, in very different degrees. It is not, however, found to bear a proportion to any other quality of bodies.

All the properties of caloric, which have been hitherto described, belong to it when in a free or uncombined form; for it continues to produce the sensation of heat and to expand the mercury of the thermometer. In the instances of its agency, also, that have been mentioned, no permanent change of form or of properties is effected in the bodies which have imbibed caloric. A bar of iron, after being expanded by heat, returns on cooling to the same state as before, and exhibits all its former qualities. In certain cases, however, caloric is absorbed by bodies, with the loss of its distinguishing properties. It can then be no longer discovered by our senses or by the thermometer: and it produces important and sometimes permanent changes in the bodies into which it enters.

Those effects of caloric, in the production of which it loses its distinguishing properties, may be classed under two general heads.

I. All bodies, in passing from a denser to a rarer state, absorb caloric.—Thus solids, during liquefaction, imbibe a quantity of caloric, which ceases to be apparent to our senses or to the thermometer: or, as it has been termed, becomes latent. In a similar manner, solids and liquids, during their conversion into vapours or gases, render latent a quantity of caloric, which is essential to the elasticity of the new product. In common language, cold is, in such cases, said to be produced; but by the production of cold we are to understand, in philosophical language, nothing more than the passage of

caloric from a free to a latent form.

II. All bodies, by an increase of density, evolve or give out caloric, which passes from a latent to a free state.—The simplest illustration of this law is in the effect of hammering a piece of metal, which may thus be intensely heated, while all that is effected is an augmentation of its density. Liquids by becoming solids, or gases by conversion into liquids, also, evolve caloric, or produce an increase of temperature. A pound of water, condensed from steam, will render 100 pounds of water at 50° warmer by 11°; whereas a pound of boiling water will produce the same rise of temperature in no more than about 13½ pounds. This is owing to the much greater quantity of caloric, existing in a pound of steam, than in a pound of boiling water, though steam and boiling water affect the thermome-

ter in precisely the same degree.

It is a question which has excited considerable interest among philosophers, whether caloric, when thus absorbed and rendered latent, enters into chemical combination, or is merely united by the same kind of ties as that portion of caloric that produces the temperature of bodies. Does ice, for example, when changed into water, form a chemical union with caloric, similar to that which exists between potash and sulphuric acid? Such appears to have been the opinion of Dr. Black, who, by the powers of an original and well directed genius, discovered the greater number of those facts that form the groundwork of the theory of latent heat. The resemblance. however, between chemical union and the disappearance of caloric, which, on first view, appears extremely striking, will be found, it must be confessed, less close on a nearer examination. For caloric may be made to quit those bodies, into which it has entered with the loss of its peculiar properties, merely by reducing their temperature; whereas chemical combinations in general cannot be destroyed, except by the interference of more energetic affinities. In opposition to the foregoing theory, it has been contended that the absorption of caloric by bodies is a consequence of what has been called a change of their capacity. Thus ice, it is supposed, in becoming water, has its capacity for caloric increased, and the absorption of caloric is a consequence of this increased capacity. theory, however, is deficient, inasmuch as it fails to explain what is the cause of that change of form, which is assumed to account for the increase of capacity. Notwithstanding this obvious objection, I have retained the term capacity to express in the abstract, that power by which bodies absorb and render latent different quantities of caloric; or the property of requiring more or less caloric for raising their temperature an equal number of degrees. The absorption of caloric, then, will always be owing to an increase, and its evolution to a decrease, of capacity. The use of these terms may be exemplified by a slight change of the perspicuous language of Dr. Crawford. "The capacity for containing caloric\*," he observes, "and the absolute caloric contained, are distinguished as a force from the subject upon which it operates. When we speak of the absolute caloric, we mean an unknown principle, which is retained in the body by the possession of this power; and when we speak of the temperature, we consider the unknown principle as producing certain effects upon the thermometer."

As the capacities of bodies determine their absolute quantities of caloric, it seems reasonable to conclude, that if we can ascertain how much caloric a body absorbs or gives out in changing its form, and in what proportion its capacity is at the same time altered, we may deduce the absolute quantity of heat which it contains. Now it will be afterwards shown that the heat, evolved by water in freezing, is equal to 140°; and the capacity of water has been stated to bear to that of ice the proportion of 10 to 9. Water, then, in becoming ice, must give out 1 of its whole caloric, and as this amounts to 140°, ten times 140 (or 1400°) is the whole quantity of caloric in water at the temperature of 32°: and deducting 140 from 1400, we have 1260° for the caloric contained in the ice itself. This method of determining the problem appears, however, to me, to be liable to several objections, which it would take up too much room to state in this place, and which I have elsewhere urged at considerable lengtht.

These general observations I have deemed it necessary to make, with a view of connecting together the propositions respecting caloric, and the experiments illustrating them, that form the subject of the following sections. The inquiry respecting heat is one which presents a boundless field for interesting speculation; and it would have been easy to have extended very considerably the discussion of its nature and properties. But in this work, I have no farther object than to lead the student, by easy steps, to a knowledge of what has been actually determined by experiment, or strictly and legitimately

deduced from it.

<sup>\*</sup> Dr. Crawford on Heat, p. 8. † Manchester Memoirs, v.; or Phil. Mag.

### SECTION II.

# Rlustrations of the Effects of Free Caloric.

I. Caloric expands all bodies.—The expansion of liquids is shown by that of the mercury of a thermometer, or by immersing in hot water a glass matrass (pl. i. fig. 4), filled up to a mark in the neck, with spirit of wine, tinged with any colouring substance. rit expands immediately when heated, and would overflow if not placed in a cooler situation. The degree of expansion produced in different liquids, by similar elevations of temperature, varies very considerably. Thus water expands much more than mercury, and alcohol more than water. This difference of expansibility is even sufficiently striking to appear in a remarkable degree, when we immerse, in water heated to 150°, three equal glass vessels of the shape of thermometer tubes containing, the one mercury, the other water, and the third spirit of wine. The spirit will begin to escape from the aperture of the vessel, before the mercury has ascended far in the stem\*. The expansion of aeriform bodies is shown, by holding, near the fire, a bladder filled with air, the neck of which is closely tied, so as to prevent the enclosed air from escaping. The bladder will soon be fully distended, and may even be burst by continuing and increasing the heat. All aëriform bodies undergo the same expansion by the same additions of heat, or 483 part of their bulk for each degree of Fahrenheit's thermometer, between the freezing and boiling points. The expansion of solids is evinced, by heating a rod of iron, of such a length as to be included, when cold, between two points, and the diameter of which is such, as barely to allow it to pass through an iron ring. When heated, it will have become sensibly longer; and it will be found incapable of passing through the ring. This property of metals has been applied to the constructing of an instrument for measuring temperature, called a pyrometer, a neat and distinct representation of which is given in the first volume of "Chemical Conversations;" and also, by M. Bréguet, to the formation of a very sensible metallic thermometer t.

The degree of expansion is not the same for all solids, and even differs materially in substances of the same class. Thus the metals expand in the following order, the most expansible being placed first; zinc, lead, tin, copper, bismuth, iron, steel, antimony, palladium, platina ‡.

All the above bodies return again, on cooling, to their former dimensions:

II. Construction of the thermometer founded on the principle of expansion.—The thermometer is an instrument of so much impor-

See a table of the expansions of liquids in the Appendix.

<sup>†</sup> Ann. de Chim. et. Phys. v. 312. ‡ See the table in the Appendix.

tance, that it may be expedient to explain the construction of the different kinds which are required in chemical researches.

The instrument employed by Sanctorio, to whom the invention of the thermometer is generally ascribed, was of a very simple kind, and measured variations of temperature by the variable expansion of a confined portion of air. To prepare this instrument, a glass tube (pl. i. fig. 9) is to be provided, eighteen inches long, open at one end, and blown into a ball at the other. On applying a warm hand to the ball, the included air expands and a portion is expelled through the open end of the tube. In this state, the aperture is quickly immersed in a cup filled with any coloured liquid, which ascends into the tube, as the air in the ball contracts by cooling. The instrument is now prepared. An increase of temperature forces the liquor down the tube; and, on the contrary, the application of cold causes its ascent. These effects may be exhibited, by alternately applying the hand to the ball, and then blowing on it with a pair of bellows. By the application of a graduated scale, the amount of the expansion may be measured.

The ball of the above instrument, it must be obvious, cannot be conveniently applied to measure the temperature of liquids. adapting it to this purpose, a slight variation may be made in its construction, as represented fig. 8, a. To prepare this instrument, a small spherical glass vessel is to be about one 6th or one 4th filled with any coloured liquid. The tube, open at both ends, is then to be cemented into the neck, with its lower aperture beneath the surface of the fluid. The expansion of the included air drives the liquid up the stem, to which we may affix a graduated scale, corresponding with that of a common mercurial thermometer. Other modifications have also been made by different philosophers. One of the most useful and simple forms is represented fig. 8, b. It consists merely of a tube of very small bore, from 9 to 12 inches long, at one end of which is blown a ball, from half an inch to an inch in diameter, which is afterwards blackened by paint, or by the smoke of a candle. A small column of coloured liquid, about an inch in length, is then introduced, by a manipulation similar to that already To fit the instrument for use, this column ought to be described. stationary, about the middle of the tube, at the common temperature of the atmosphere. The slightest variation of temperature occasions the movement of the coloured liquid; and a scale of equal parts measures the amount of the effect.

An insuperable objection, however, to the air thermometer, as thus constructed, is, that it is affected, not only by changes of temperature, but by variations of atmospheric pressure. Its utility consists in the great amount of the expansion of air, which, by a given elevation of temperature, is increased in bulk above twenty times more than mercury. Hence it is adapted to detect minute changes of temperature, which the mercurial thermometer would scarcely discover.

An important modification of the air thermometer has been invented by Mr. Leslie, and employed by him, with great advantage, in his interesting researches respecting heat. To this instrument he

has given the name of, the Differential Thermometer. Its construction is as follows: "Two glass tubes of unequal length, each terminating in a hollow ball, and having their bores somewhat widened at the other ends (a small portion of sulphuric acid, tinged with carmine, being introduced into the ball of the longer tube), are joined together by the flame of a blow-pipe, and afterwards bent nearly into the shape of the letter U (see fig. 7), the one flexure being made just below the joining, where the small cavity facilitates the adjustment of the instrument. This, by a little dexterity, is performed, by forcing, with the heat of the hand, a few minute globules of air from the one cavity into the other. The balls are blown as equal as the eye can judge, and from four 10ths to seven 10ths of an inch di-The tubes are such as are drawn for thermometers, only with wider bores; that of the short one, to which the scale is affixed, must have an exact calibre of a 50th, or a 60th, of an inch. The bore of the long tube need not be so regular, but should be visibly larger, as the coloured liquid will then move quicker under any impression. Each leg of the instrument is from three to six inches in height, and the balls are from two to four inches apart.

"A moment's attention to the construction of this instrument will satisfy us, that it is affected only by the difference of heat in the corresponding balls; and is calculated to measure such difference with peculiar nicety. As long as both balls are of the same temperature, whatever this may be, the air contained in both will have the same elasticity, and, consequently, the intercluded coloured liquor, being pressed equally in opposite directions, must remain stationary. But if, for instance, the ball which holds a portion of the liquor be warmer than the other, the superior elasticity of the confined air will drive the liquid forwards, and make it rise, in the opposite branch, above the zero, to an elevation proportional to the excess of elasticity, or of heat." The amount of the effect is ascertained by a graduated scale, the interval between freezing and boiling being distinguished into 100 equal degrees. This instrument, it must be obvious, cannot be applied to measure variations in the temperature of the surrounding atmosphere, for the reason already assigned. It is peculiarly adapted to ascertain the difference of the temperatures of two contiguous spots in the same atmosphere; for example, to determine the heat in the focus of a reflector.

Thermometers, filled with spirit of wine (a liquid which has not been congealed by any degree of cold hitherto produced), are best adapted to the measurement of very low temperatures, at which mercury would freeze. The amount of the expansion of alcohol, also, which exceeds that of mercury above eight times, fits it for ascertaining very slight variations of temperature. But it cannot be applied to measure high degrees of heat; because the conversion

of the spirit into vapour would burst the instrument.

The fluid, best adapted for filling thermometers, is mercury, which, though it expands less in amount than air, or alcohol, still undergoes this change to a sufficient degree; and, in consequence of its Vol. I.—I.

difficult conversion into vapour, may be applied to the admeasurment of more elevated temperatures. As a considerable saving of expense will accrue to the experimentalist, who is able to construct mercurial thermometers, I shall offer some rules for this purpose. In general, however, I should deem it preferable merely to superintend their construction, and to be satisfied, by actual inspection, that the necessary accuracy is observed; because much time must be unavoidably lost, in acquiring the manual skill which is essential to

construct them neatly.

Thermometer tubes may be had at the glass-house, and of various philosophical instrument makers. In purchasing them, those should be rejected that are not hermetically sealed at both ends; because the smallest condensation of moisture, which must take place when air is freely admitted within the tube, is injurious to the accuracy of the instrument. A small bottle of elastic gum should be provided, in the side of which a brass valve is fixed, or a piece of brass perforated by a small hole, to be occasionally stopped by the hand. blow-pipe is also an essential part of the apparatus; and, in addition to one of the ordinary kind, it will be found useful to have one which is supplied with air by a pair of double bellows, worked by the foot.

Before proceeding to the construction of the thermometer, it is necessary to ascertain, that the tube is of equal diameter in different parts. This is done by breaking off both of the sealed ends, immersing one of them an inch or two deep in clean and dry mercury, and then closing the other end with the finger. On withdrawing the tube from the mercury, a small column of that fluid remains in it. the length of which is to be examined, by laying the tube horizontally on a graduated ruler\*. By inclining the tube, this column may be gradually moved through its whole length; and if the tube be of uniform bore, it will measure the same in every part. Such a degree of perfection, however, is scarcely ever to be observed throughout tubes of considerable length; but, in general, a portion of the tube will be found perfect, of sufficient length for a thermometer, and this part is to be broken off.

On one end of the tube let the neck of the elastic bottle be firmly tied; and let the other end be heated by the flame of the blow-pipe, till the glass softens. The softened part must then be pressed, by a clean piece of metal, into the form of a rounded button; and to this the flame of the lamp must be steadily applied, till it acquires a white heat, and seems about to enter into fusion. To prevent its falling on one side, the tube, during this time, must be constantly turned round by the hand. When the heated part appears perfectly soft, remove it quickly from the lamp, and, holding the tube vertically, with the elastic bottle uppermost, press this last gently with the hand. The glass will be blown into a small ball, but not into one.

<sup>\*</sup> If the tube be of an extremely small bore, the mercury will not enter, and must be drawn in by the action of the elastic bottle, and not by the mouth,

sufficiently thin for the purpose. To this the flame of the lamp must again be applied, turning it quickly round; and, on a second or third repetition of the process of blowing, the ball will be completely formed. The proportion of the size of the ball to the bore of the

tube can only be learned by some experience.

To fill the ball, which has been thus formed, with mercury, the air must first be expelled by holding it over the flame of an Argand's lamp, and then quickly immersing the open end of the tube in very clean and dry quicksilver. As the ball cools the mercury will ascend, and will partly fill it. Let a paper funnel be tied firmly over the open end of the tube; into this pour a small portion of quicksilver, and apply the heat of the lamp to the ball. Any remaining portion of air will thus be expelled; and if the heat be raised so as to boil the mercury, the ball and stem will be filled with mecurial vapour, the condensation of which, on removing the ball from the lamp, will occasion a pretty complete vacuum. Into this vacuum, quicksilver will descend from the paper cone; and the instrument will be completely filled. But for the purpose of a thermometer, it is necessary that the mercury should rise only to a certain height of the stem; and a few drops may, therefore, be expelled by cautiously applying the heat of the lamp. To estimate whether the proper quantity of quicksilver has been left in the instrument, immerse the ball first in ice-cold water, and then in the mouth. The space between these two points will comprise 63 degrees, or pretty nearly one third of the whole space between the freezing and boiling points of water. If the empty part of the tube exceeds, in length, about three times the portion thus filled by the expanded quicksilver, we may proceed (when an instrument is wanted with a scale including only from 32° to 212°) to seal it hermetically: which is done as follows: The part to be sealed is first heated with the blow-pipe, and drawn out to a fine capillary tube: the bulb is then heated, till a few particles of quicksilver have fallen from the top of the tube: at this moment, the flame of another candle is directed, by the blowpipe, on the capillary part of the tube, the candle is withdrawn from the ball, and the tube is sealed, at the instant when the mercury begins to descend. If this operation has been skilfully performed, so as to leave no air in the tube, the whole of the tube should be filled with quicksilver on holding the instrument with the ball uppermost.

To have very large degrees, the ball must bear a considerable proportion to the tube; but this extent of scale cannot be obtained without sacrificing, in some measure, the sensibility of the instrument. The whole of the process of constructing thermometers neatly and accurately, is connected with the possession of manual skill, which practice only can confer; and it is scarcely possible, without the most tedious minuteness, to describe all the necessary precautions and manipulations. These will readily suggest themselves to a person who carries the above instructions into effect.

In graduating thermometers, the first step consists in taking the two fixed points. The freezing point is ascertained, by immersing,

in thawing snow or ice, the ball and part of the stem; so that the mercury, when stationary, shall barely appear above the surface. At this place let a mark be made with a file. In taking the boiling point, considerable caution is required; and, for reasons which will afterwards be stated, attention must be paid to the state of the barometer, the height of which, at the time, should be precisely 29.8. A tin vessel is to be provided, (for according to Gay Lussac\*, one of glass leads to erroneous results,) four or five inches longer than the thermometer, and furnished with a cover, in Through one of these, the thermometer stem which are two holes. must be passed (the bulb being within the vessel), so that the part; at which the boiling point is expected, may be just in sight. other hole may be left open; and the cover being fixed in its place, the vessel, containing a few inches of water at the bottom, is to beset on the fire. The thermometer will presently be wholly surrounded by steam; and when the mercury becomes stationary in the stem, its place must be marked. The scale of Fahrenheit is formed by transferring the intermediate space to paper by a pair of compasses, and dividing it into 180°, the lowest being called 32°, and the highest 212°. The scale of other countries, however, differs considerably; but these variations do not prevent the comparison of observations with different instruments, when the freezing and boiling points of water are agreed upon as fixed data. In the Appendix, rules will be given for converting the degrees of other scales to that of Fahrenheit.

III. The dilatations and contractions of the fluid in the mercurial thermometer, are nearly proportional to the quantities of caloric, which are communicated to the same homogeneous bodies, or separa-

ted from them, so long as they retain the same form.

Thus a quantity of caloric, required to raise a body 20° in temperature, by the mercurial thermometer, is nearly double that which is required to raise it 10°. Hence there appears to be a pretty accurate proportion between the increments or decrements of heat, and the increments and decrements of expansion in the mercury of . a thermometer. On this principle, if equal quantities of hot and cold water be mixed together, and a thermometer be immersed in the hot water, and also in the cold, previously to the mixture, the instrument should point, after the mixture, to the arithmetical mean, or to half the difference of the separate heats, added to the less or subtracted from the greater. This will be proved to be actually the fact, by the following experiment. Mix a pound of water at 172° with a pound at S2°. Half the excess of the caloric of the hot water will pass to the colder portion; that is, the hot water will be cooled 70°, and the cold will receive 70° of temperature; therefore 172-70, or 32 + 70 = 102, will give the heat of the mixture. To attain the arithmetical mean exactly, several precautions must be observedt.

<sup>\* 82</sup> An. de Ch. 174, and 7 An. de Ch. et Phys. 307. † See Crawford on Animal Heat, p. 95, &c.

The experiments of De Luc, however, have shown, that the ratio of expansion does not, strictly, keep pace with the actual increments of temperature; and that the amount of the expansion increases with the temperature. Thus if a given quantity of mercury, in being heated from 32 to 122°, the first half of the scale, be expanded 14 parts, in being raised from 122 to 212, the higher half, it will be

expanded 15 parts.

From the inquiries of Mr. Dalton, it appears to follow, that the irregularity of the expansion of mercury is considerably greater than has been stated by De Luc. By the common mercurial thermometer, we cannot ascertain the true rate of expansion in quicksilver; for it must be obvious that the expansion of the glass ball, in which it is contained, must considerably affect the result. If the capacity of the ball remained unaltered, we should then be able to determine the actual rate of expansion; but by an increase of temperature its capacity is enlarged, and space is thus found, within the ball, for the expansion of that mercury, which would otherwise be driven into the tube. By knowing the rate of expansion in glass itself, we can correct this error; but a small error in this datum will lead us considerably wrong as to the true expansion of quicksilver. The real expansion of mercury in glass is greater than the apparent, by the expansion of the glass itself.

Making due correction for this circumstance, Mr. Dalton has been led to conclude from his experiments, that notwithstanding the apparent diversities of expansion in different fluids, they all actually expand according to the same law; viz. that the quantity of expansion is as the square of the temperature from their respective freezing points, or from their points of greatest density. If then a thermometer be constructed, with degrees corresponding to this law, they will be found to differ very considerably from those of the common mercurial thermometer, in which the space between freezing and boiling is divided into 180 equal parts. In the Appendix will be found a table showing the correspondence between the old scale

and the new one constructed on Mr. Dalton's principle.

IV. Uncombined caloric has a tendency to an equilibrium. Any number of different bodies, at various temperatures, if placed under similar circumstances of exposure, all acquire a common temperature. Thus, if in an atmosphere at 60°, we place iron filings heated to redness, boiling water, water at 32°, and various other bodies of different temperatures, they will soon affect the thermometer in the ame degree. The same equalization of temperature is attained, hough less quickly, when a heated body is placed in the vacuum of an air-pump. The rate of cooling in air is to that in vacuo, the temperatures being equal, nearly as five to two.

II. Motion of Free Caloric.—1. Its Radiation.—2. Its Passage through Solids and Fluids.

Caloric escapes from bodies in two different modes.—Part of it finds its way through space, independently of other matter, and with

immeasureable velocity. In this state it has been called, radiant heat, or radiant caloric.

RADIANT CALORIC exhibits several interesting properties.

1. Its reflection. (a) Those surfaces, that reflect light most perfectly, are not equally adapted to the reflection of caloric. Thus, a glass mirror, which reflects light with great effect when held before a blazing fire, scarcely returns any heat, and the mirror itself becomes warm. On the contrary, a polished plate of tin, or a silver spoon, when similarly placed, reflects, to the hand, a very sensible degree of warmth; and the metal itself remains cool. Metals, therefore, are much better reflectors of caloric than glass; and they possess this property, exactly according to their degree of polish.

(b) Caloric is reflected according to the same law that regulates the reflection of light. This is proved by an interesting experiment of M. Pictet; the means of repeating which may be attained at a moderate expense. Provide two reflectors of planished tin (a and b, fig. 45), which may be 12 inches diameter, and segments of a sphere of nine inches radius. Parabolic mirrors are still better adapted to the purpose; but their construction is less easy. Each of these must be furnished, on its convex side, with the means of supporting it in a perpendicular position on a proper stand. Place the mirrors opposite to each other on a table, at the distance of from six to 12 feet. Or they may be placed in a horizontal position, as represented in the fourth plate to Sir H. Davy's Chemical Philosophy, an arrangement in some respects more convenient. In the focus of one, let the ball of an air thermometer, c, or (which is still better) one of the balls of a differential thermometer, be situated; and in that of the other, suspend a ball of iron, about four ounces in weight, and heated below ignition, or a small matrass of hot water, d; having previously interposed a screen before the thermometer. Immediately on withdrawing the screen, the depression of the column of liquid, in the air thermometer, evinces an increase of temperature in the instrument. In this experiment, the caloric flows first from the heated ball to the nearest reflector; from this it is transmitted, in parallel rays, to the surface of the second reflector, by which it is collected into a focus on the instrument. This is precisely the course that is followed by radiant light; for if the flame of a taper be substituted for the iron ball, the image of the candle will appear precisely on that spot (a sheet of paper being presented for its reception) where the rays of caloric were before concentrated.

(c) When a glass vessel, filled with ice or snow, is substituted for the heated ball, the course of the coloured liquid in the thermometer will be precisely in the opposite direction; for its ascent will show, that the air in the ball is cooled by this arrangement. This experiment, which appears, at first view, to indicate the reflection of cold, presents, in fact, only the reflection of heat in an opposite direction; the ball of the thermometer being, in this instance, the hotter body. "And since heat emanates from bodies in quantities greater as their temperature is higher, the introduction of a cold

body into the focus of one mirror, necessarily diminishes the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in the focus of the one, would diminish the quantity of light in the focus of the other\*."

(d) In Mr. Leslie's "Enquiry into the Nature, &c. of Heat," a variety of important experiments are detailed, which show the influence of covering the reflectors with various substances, or of mechanically changing the nature of their surfaces, on their power of

returning caloric.

2. Caloric is refracted, also, according to the same law that regutes the refraction of light. This interesting discovery we owe to lates the refraction of light. Dr. Herschell, whose experiments and apparatus, however, cannot be understood without the assistance of a plate. For this reason, I refer to his paper in the 90th vol. of the Philosophical Transactions, or in the 7th vol. of the Philosophical Magazine.

3. The nature of the surface of bodies has an important influence

over their power of radiating caloric.

To exhibit this influence experimentally, let a canister of planished block tin, forming a cube of six or eight inches, be provided, having an orifice at the middle of its upper side, from half an inch to an inch diameter, and the same in height. This orifice is intended to receive a cap having a small hole, through which a thermometer is inserted, so that its bulb may reach the centre of the canister. Let one side of the canister be covered with black paint; destroy the polish of another side, by scratching it with sand-paper; tarnish a third with quicksilver; and leave the fourth bright. Then fill the vessel with boiling water. The radiation of caloric from the blackened side is so much more abundant than from the others, as to be even sensible to the hand. Place it before a reflector (fig. 45), in lieu of the heated iron ball already described. The thermometer, in the focus of the second reflector, will indicate the highest temperature, or most copious radiation of caloric, when the blackened side is presented to the reflector; less when the tarnished or scratched side is turned towards it; and least of all from the polished side.

These varieties in the radiating power of different surfaces, are attended, as might be expected, with corresponding variations in the rate of cooling. If water in a tin vessel, all of whose sides are polished, cools through a given number of degrees in eighty-one minutes, it will descend through the same number in seventy-two minutes, if the surface be tarnished with quicksilver. Water, also, enclosed in a clean and polished tin ball, cools about twice more slowly than water in the same ball covered with oiled paper. Blackening the surface with paint, or even a thin coat of varnish, on the same principle, accelerates greatly the rate of cooling. These facts teach us, that vessels, in which fluids are to be long kept hot should have their surfaces brightly polished; and they explain, among other things,

the superiority of metallic tea-pots over those of earthen ware.

Davy's Chem. Philos. p. 206.

5. Radiant caloric is absorbed with different facility by different surfaces. This is only stating, in other terms, that surfaces are enclowed with various powers of reflecting caloric since the power of absorbing caloric is precisely opposite to that of reflecting it. Hence the best reflectors of heat will absorb the least. It may be proper, however, to offer some illustrations of the principle under this form.

(a) Expose the bulb of a sensible thermometer to the direct rays of the sun. On a hot summer's day it will probably rise, in this climate, to 108°\*. Cover it with Indian ink, and again expose it in a similar manner. During the evaporation of the moisture it will fall; but as soon as the coating becomes dry, it will ascend to 118°, or upwards, of Fahrenheit, or 10° higher than when uncovered with the pigment. This cannot be explained by supposing that the black coating is gifted with the power of retaining caloric, and preventing its escape; because from experiments already related, it appears, that a similar coating accelerates the cooling of a body to which it is applied.

(b) Colour has considerable influence over the absorption of caloric. This is shown by the following very simple experiment of Dr.

Franklin.

On a winter's day, when the ground is covered with snow, take our pieces of woollen cloth, of equal dimensions but of different colours, viz. black, blue, brown, and white, and lay them on the surface of the snow, in the immediate neighbourhood of each other. In a few hours, the black cloth will have sunk considerably below the surface; the blue almost as much; the brown evidently less; and the white will remain precisely in its former situation. Thus it appears, that the sun's rays are absorbed by the dark coloured cloth, and excite such a durable heat, as to melt the snow underneath; but they have not the power of penetrating the white. Hence the preference generally given to dark coloured cloths during the winter season, and to light coloured ones in summer, appears to be founded on reason.

(c) This experiment has been varied by sir H. Davy, in a manner which may be repeated at any season of the year. Take six similar pieces of sheet copper, each about an inch square, and colour the one white, another yellow, a third red, the fourth green, the fifth blue, and the sixth black. On the centre of one side of each piece, put a small portion of a mixture of oil and wax, or cerate, which melts at about 76°. Then expose their coloured surfaces, under precisely equal circumstances, to the direct rays of the sun. The cerate on the black plate will begin to melt perceptibly before the red; the blue next; then the green and the red; and, lastly, the yellow. The white will scarcely be affected, when the black is in complete fusion.

Caloric passes, also, but more slowly, through solid and liquid bodies, which are then termed conductors of caloric.

1. Solid bodies convey heat in all directions, upwards, downwards, and laterally; as may be shown, by heating the middle of an

iron rod, and holding it in different directions.

2. Some bodies conduct caloric much more quickly than others. Coat two rods, of equal length and thickness, the one of glass, the other of iron, with wax, at one end of each only; and then apply heat to the uncoated ends. The wax will be melted vastly sooner from the end of the iron rod, than from the glass one; which shows,

that iron conducts heat more quickly than glass.

Even the different metals possess very different powers of conducting caloric. An approximation to the degree in which they possess this property, may be attained by the following method, originally employed by Dr. Ingenhouz. Procure several solid cylinders, or rods, of the same size and shape, but of different metals. They may be six inches long, and one 4th of an inch in diameter. Coat them, within about an inch of one end, with bees-wax, by dipping them into this substance when melted, and allowing the covering to congeal. Let an iron heater be provided, in which small holes have been drilled, that exactly receive the clean ends of the cylinders. After heating it below ignition, insert the cylinders in their places. The conducting power may be estimated by the length of wax coating melted from each in a given time. According to the experiments of Dr. Ingenhouz, the metals may be arranged in the following order: Silver possesses the highest conducting power; next, gold; then copper and tin, which are nearly equal; and, below these, platina, iron, steel, and lead, which are greatly inferior to the rest.

It is chiefly owing to the different conducting powers of bodies, that they affect us, when we touch them, with different sensations if cold. Thus, if we apply the hand in succession to a number of bodies (as a piece of wood, another of marble, &c.), they appear cold in very different degrees. And as this sensation is occasioned by the passage of caloric out of the hand into the body which it touches, that body will feel the coldest, which carries away heat the most quickly; or which, in other words, is the best conductor. For the same reason, of two bodies which are heated to the same degree, and both considerably above the hand, the best conductor is the hottest to the touch. Thus the money in our pockets often feels hotter than the clothes which contain it.

3. Liquid and aëriform bodies convey heat on a different principle from that observed in solids, viz. by an actual change in the situation of their particles. That portion of the fluid, which is nearest to the source of heat, is expanded, and becoming specifically lighter, ascends, and is replaced by a colder portion from above. This, in its turn, becomes heated and dilated, and gives away to a second colder portion; and thus the process goes on, as long as the fluid is capable of imbibing heat.

(a) Take a glass tube, eight or 10 inches long, and about an inch in diameter. Pour into the bottom part, for about the depth of an inch, a little water tinged with litmus, and then fill up the tube with

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common water, pouring on the latter extremely gently, so as to keep the two strata quite distinct. If the upper part of the tube be first heated, the coloured liquor will remain at the bottom; but if the tube be afterwards heated at the bottom, the infusion will ascend,

and will tinge the whole mass of fluid.

(b) Into a cylindrical glass jar, four inches diameter, and 12 or 14 deep, let a circular piece of ice be fitted 34 inches thick, and of rather less diameter than the jar. Or water may be poured into the jar to the depth of 31 inches, and allowed to congeal by exposure to a freezing atmosphere, or by surrounding it with a mixture of snow and salt. The ice is to be secured in its place by two slips of wood, crossing each other like two diameters of a circle, set at right angles to each other. Pour, over the cake of ice, water of 32° temperature, to the depth of two inches; and on its surface let there float a shallow circular wooden box, perforated with holes. From the cock of a tea-urn, filled with boiling water, and raised so that its spout may be above the top of the jar, suspend a number of moistened threads, the lower ends of which must rest on the surface of the box. By this arrangement, when the cock is turned, the hot water will trickle down the threads, and will have its fall considerably broken. It will then spread over the surface of the box, and pass through the perforated holes to the cold water beneath, over which it will float without mixing with it. Let the jar be thus com-pletely filled with hot water. The ice will remain unmelted for several hours at the bottom of the vessel.

(c) Fill a similar jar with hot water; and, having provided a cake of ice, of equal size with the former one, let it be placed on the surface of the water. In about three minutes, the whole will be melted. Both these experiments are more striking, if the water, used for forming the cakes of ice, be previously coloured with litmus; for, in the latter experiment, the descending currents of cold water are

thus made apparent.

(d) These experiments may be varied, by freezing, in the bottom of a tube one inch wide, a portion of water, about two inches in depth. Then fill the tube with water of the common temperature, and hold it inclined over an Argand's lamp, so that the upper portion only of the tube may be heated. When thus disposed, the water may be made to boil violently at the surface, and yet the ice will not be melted. But if the experiments be reversed, and (the ice floating on the surface) heat be applied to the bottom of the tube, the ice

will be liquefied in a few seconds.

(e) Substituting water of the temperature of 41° for the boiling water used in experiment (c), Count Rumford found, that, in a given time, a much greater quantity of ice was melted by the cooler water. This appears, on first view, rather paradoxical. The fact, however, is explained by a remarkable property of water, viz. that when cooled below 40° it ceases to contract, and experiences, on the contrary, an enlargement of bulk. Water, therefore, at 40° (at the bottom of which is a mass of ice at \$2°), is cooled by contact with the ice, and is expanded at the same moment. It therefore ascends, and is replaced by a heavier and warmer portion from above-

It is a consequence of the same property that the surface of a deep lake is sometimes covered with ice, even when the water below is only cooled to 40°; for the superficial water is specifically lighter than the warmer water beneath it, and retains its place, till it is changed into ice. This property of water is one of the most remarkable exceptions to the law, that bodies are expanded by an in-

crease, and contracted by a diminution, of temperature.

From these facts, Count Rumford concluded, that water is a perfect non-conductor of caloric, and that it propagates caloric in one direction, viz. upwards, in consequence of the motions which it occasions among the particles of the fluid. The Count inferred also, that if these motions could be suspended, caloric would cease to pass through water; and, with the view of deciding this question, he made the following experiments, which admit of being easily repeated. A cylindrical tin vessel must previously be provided, two inches in diameter, and 2½ inches deep, having a moveable cover, perforated with a small aperture, for transmitting the stem of a thermometer, which is to be inserted so that its bulb may occupy the centre of the vessel.

(f) Fill this vessel with water of the temperature of the atmosphere; let the cover be put in its place; and let the whole apparatus, except the scale of the thermometer, be immersed in water, which is to be kept boiling over a lamp. Observe how long a time is required to raise the water from its temperature at the outset to 180°, and remove it from its situation. Note, also, how long it takes

to return to its former temperature.

(g) Repeat the experiment, having previously dissolved in the water 200 grains of common starch. The thermometer will now require about half as long again to arrive at the same temperature. A similar retardation, and to a greater amount, is produced by the mixture of eider-down, cotton-wool, and various other substances, which are not chemically soluble in water, and which can diminish its conducting power in no other way than by obstructing the motion

of its particles.

This inference, however, respecting the complete non-conducting power of water, has been set aside by the subsequent inquiries of Dr. Thomson and Dr. Murray, especially by a most decisive experiment of the latter. To establish the conducting power of water, it was justly deemed indispensable, that caloric should be proved to be propagated through that fluid downwards. This, on actual trial. it appeared to be; but it was objected, that the sides of the containing vessel might be the conductor. To obviate this objection, Dr. Murray contrived to congeal water into the form of a jar, capable of holding liquids. This was separately filled with linseed oil and with mercury. At a proper distance below the surface, the bulb of a thermometer was placed; and on the surface of the liquid rested a flat iron vessel, containing boiling water. Under these circumstances, the thermometer invariably rose; and though it ascended only a very few degrees, yet it must be recollected, that the cooling power of the sides of the vessel would effectually prevent any considerable elevation of temperature. This experiment, in conjunction with others, decisively proves, that water is a conductor, though a slow or imperfect one, of caloric.

## SECTION III.

# Caloric the Cause of Fluidity.

I. The temperature of melting snow, or of thawing ice, is uniformly the same at all times, and in all places.—This may be ascertained by the thermometer, which will always, when immersed in liquefying ice or snow, point to 32° of Fahrenheit, whatsoever may be the height of the barometer, or the elevation, above the sea, of the place where the experiment is made\*.

II. The sensible heat, or temperature of ice, is not changed by liquefaction.—A thermometer in pounded ice stands at 32°, and at the very same point in the water which results from the liquefaction

of ice.

III. Yet ice, during liquefaction, must absorb much caloric.—Expose a pound of water at 32°, and a pound of ice at 32°, in a room, the temperature of which is several degrees above the freezing point, and uniformly the same during the experiment. The water will arrive at the temperature of the room, several hours before the ice is melted; and the melted ice will have, as before its liquefaction, the temperature of 32°. Yet the ice must, during the whole of this time, have been imbibing caloric, because (according to Experiment IV. § 2.) a colder body can never be in contact with a warmer one, without receiving caloric from it. The caloric, therefore, which has entered the ice, but is not to be found in it by the thermometer, is said to have become latent. As it is the cause of the liquefaction of the ice, it is sometimes called caloric of fluidity.

IV. The quantity of caloric that enters into a pound of ice and becomes latent, during liquefaction, may be learned by experiment. To a pound of water, at 172°, add a pound of ice at 32°. The temperature will not be the arithmetical mean (202°), but much below it, viz. 32°. All the excess of caloric in the hot water has therefore disappeared. From 172° take 32°; the remainder, 140°, shows the quantity of caloric that enters into a pound of ice during liquefaction; that is, as much caloric is absorbed by a pound of ice, during its conversion into water, as would raise a pound of water from \$2°

to 172°.

It is from the property of its uniformly absorbing the same quantity of caloric for conversion into water, that ice has been ingeniously applied, by Lavoisier and Laplace, to the admeasurement of the heat, evolved in certain operations. Let us suppose the body (from

<sup>\*</sup> Shuckburg, Philosophical Transactions, lxix.

which the caloric evolved either by simple cooling or combustion, is to be measured) to be inclosed in a hollow sphere of ice, with an opening at the bottom. When thus placed, the heat which is given out, will be all employed in melting the ice; and will produce this effect in direct proportion to its quantity. Hence the quantity of ice, which is converted into water, will be an accurate measure of the caloric, that is separated from the body submitted to experiment. In this way, Lavoisier ascertained that equal weights of iderent combustible bodies melt, by burning, very different weights of ice. The apparatus which he employed for this purpose, he has called the calorimeter. Its construction can scarcely be understood without the plate, which accompanies the description in his "Elements of Chemistry;" and I consider it unnecessary to copy it into this work, because the instrument is liable to several causes of inaccuracy.

V. Other examples of the absorption of caloric, during the liquefaction of bodies, are furnished by the mixture of snow and nitric acid, or of snow and common salt, both of which, in common lan-

guage, produce intense cold.

1. Dilute a portion of nitric acid with an equal weight of water; and, when the mixture has cooled, add to it a quantity of light freshfallen snow. On immersing the thermometer in the inixture, a very considerable reduction of temperature will be observed. This is owing to the absorption, and intimate fixation, of the free caloric of

the mixture, by the liquefying snow.

2. Mix quickly together equal weights of fresh-fallen snow at 32°, and of common salt cooled, by exposure to a freezing atmosphere, down to 32°. The two solid bodies, on admixture, will rapidly liquefy; and the thermometer will sink 32°, or to 0; or, according to Sir C. Blagden, to 4° lower\*. To understand this experiment, it must be recollected, that the snow and salt, though at the freezing temperature of water, have each a considerable portion of uncombined caloric. Now salt has a strong affinity for water; but the union cannot take place while the water continues solid. In order, therefore, to act on the salt, the snow absorbs all the free caloric required for its liquefaction; and during this change, the free caloric, both of the snow and of the salt, amounting to 32°, becomes latent, and is concealed in the solution. This solution remains in a liquid state at 0, or 4° below 0 of Fahrenheit; but if a greater degree of cold be applied to it, the salt separates in a concrete form.

3. Most neutral salts, also, during solution in water absorb much caloric; and the cold, thus generated, is so intense as to freeze water, and even to congeal mercury. The former experiment, however (viz. the congelation of water), may easily be repeated on a summer's day. Add to 32 drachms of water, 11 drachms of muriate of ammonia, 10 of nitrate of potash, and 16 of sulphate of soda, all finely powdered. The salts may be dissolved separately, in the order set down. A thermometer, put into the solution, will show,

<sup>\*</sup> Philosophical Transactions, lxxviii 281.

that the cold produced is at, or below, freezing; and a little water, in a thin glass tube, being immersed in the solution, will be frozen in a few minutes. Various other freezing mixtures are described in Mr. Walker's papers in the Philosophical Transactions for 1787, 88, 89, 95, and 1801. Of these the table, given in the Appendix, for which I am indebted to the obliging communication of the author, contains an arranged abstract.

4. Crystallized muriate of lime, when mixed with snow, produces a most intense degree of cold. This property was discovered some years ago by M. Lovitz, of St. Petersburg, and has been since applied, in this country, to the congelation of mercury on a very extensive The proportions which answer best, are about equal weights of the salt finely powdered, and of fresh-fallen and light snow. mixing these together, and immersing a thermometer in the mixture, the mercury sinks with great rapidity. For measuring exactly the cold produced, a spirit-thermometer, graduated to 50° below 0 of Fahrenheit, or still lower, should be employed. A few pounds of the salt are sufficient to congeal a large mass of mercury. By means of 13 pounds of the muriate, and an equal weight of snow, Messrs. Pepys and Allen froze 56 pounds of quicksilver into a solid The mixture of the whole quantity of salt and snow, however, was not made at once, but part was expended in cooling the materials themselves.

On a small scale it may be sufficient to employ two or three pounds of the salt. Let a few ounces of mercury, in a very thin glass retort, be immersed, first, in a mixture of one pound of each; and, when this has ceased to act, let another similar mixture be prepared. The second will never fail to congeal the quicksilver.

In plate iv. fig. 42, a very simple and cheap apparatus is represented, which I have generally employed to freeze mercury.

dimensions will be given in the description of the plates\*.

The salt thus expended may be again evaporated, and crystallized for future experiments.

The reader, who wishes for farther particulars respecting these experiments, is referred to the Philosophical Magazine, iii. 76.

VI. On the contrary, liquids, in becoming solid, evolve or give out caloric, or, in common language, produce heat.

1. Water, if kept perfectly free from agitation, may be cooled. down several degrees below 32°; but, on shaking it, it immediately

congeals, and the temperature rises to 32°.

2. Expose to the atmosphere, when at a temperature below freezing (for example, at 25° of Fahrenheit), two equal quantities of water, in one only of which about a fourth of its weight of common salt has been dissolved. The saline solution will be gradually cooled, without freezing, to 25°. The pure water will gradually descend to 32°, and will there remain stationary a considerable time before it con-Yet while thus stationary, it cannot be doubted, that the pure water is yielding caloric to the atmosphere, equally with the

saline solution; for it is impossible that a warmer body can be surrounded by a cooler one, without imparting caloric to the latter. The reason of this equable temperature is well explained by Dr. Crawford. (On Heat, p. 80.) Water, he observes, during freezing, is acted upon by two opposite powers: it is deprived of caloric by exposure to a medium, whose temperature is below 32°; and it is supplied with caloric, by the evolution of that principle from itself, viz. of that portion which constituted its fluidity. As these powers are exactly equal, the temperature of the water must re-

main unchanged, till the caloric of fluidity is all evolved.

3. The evolution of caloric during the congelation of water, is well illustrated by the following experiment of Dr. Crawford:into a round tin vessel put a pound of powdered ice; surround this by a mixture of snow and salt in a larger vessel; and stir the ice in the inner one, till its temperature is reduced to + 4° of Fahrenheit. To the ice thus cooled, add a pound of water at 32°. One 5th of this will be frozen, and the temperature of the ice will rise from 4° to 32°. In this instance, the caloric, evolved by the congelation of one 5th of a pound of water, raises the temperature of a pound of ice 28°.

4. If we dissolve sulphate of soda in water, in the proportion of one part to five, and surround the solution by a freezing mixture, it cools gradually down to 31°. The salt, at this point, begins to be deposited, and stops the cooling entirely. This evolution of caloric during the separation of a salt, is exactly the reverse of what happens during its solution\*.

5. To a saturated solution of sulphate of potash in water, or of any salt that is insoluble in alcohol, add an equal measure of alcohol. The alcohol attracting the water more strongly than the salt retains

it, precipitates the salt, and considerable heat is produced.

### SECTION IV.

# Caloric, the Cause of Vapour.

I. Every liquid, when of the same degree of chemical purity, and under equal circumstances of atmospheric pressure, has one peculiar point of temperature, at which it invariably boils.—Thus, pure water always boils at 212°, alcohol at 176°, and ether at 98°, Fahrenheit; and, when once brought to the boiling point no liquid can be made hotter, however long the application of heat be con-tinued. The boiling point of water may be readily ascertained, by immersing the thermometer in water boiling, in a metalic vessel, over the fire. As there is some danger in applying heat directly to a vessel containing either ether or alcohol, the ebullition of these fluids may be shown by immersing the vessel containing them in water, the temperature of which may be gradually raised. The

<sup>\*</sup> Blagden, Philosophical Transactions, lxxviii. 290.

appearance of boiling is owing to the formation of vapour at the bottom of the vessel, and its escape through the heated fluid above it. That the steam, which escapes, is actually formed at the bottom, and not at the top of the water, may be seen by boiling some water in a Florence flask, or other transparent vessel, over an Argand's lamp. The bubbles of vapour will all ascend from the bottom of the vessel. A few exceptions to the fixity of the boiling point of liquids, arising chiefly from the material of which the containing vessel is composed, have lately been stated by Gay Lussac\*.

II. Steam has exactly the same temperature as boiling water,— Let a tin vessel be provided, having two holes in its cover, one of which is just large enough to admit the stem of a thermometer. Fill it partly with water, and let the bulb of the thermometer be an inch or two above the surface of the water, leaving the other aperture open for the escape of vapour. When the water boils, the thermometer, surrounded by steam, will rise to 212°, which is precisely the temperature of the water beneath: yet water, placed on a fire, continues to receive heat, very abundantly, even when boiling hot; and as this heat is not appreciable by the thermometer, it must exist in

the steam, in a latent state.

Perfectly formed steam in entirely invisible. We may satisfy ourselves of this by boiling strongly a small quantity of water in a flask; for complete transparency will exist in the upper part of the vessel. It is only when it begins to be condensed, that steam becomes visible. We have a proof also of the same fact in the thick fogs which are produced by a sudden transition from warm to cold weather; the vapour which was imperceptible at the higher temperature, being condensed and rendered visible by the lower.

III. The boiling point of the same fluid varies, under different degrees of atmospheric pressure.—Thus water, which has been removed from the fire, and has ceased to boil, has its ebullition renewed when it is placed under a receiver, the air of which is quickly exhausted by an air pump. Alcohol and ether, confined under an exhausted receiver, boil violently at the temperature of the atmosphere. In general, liquids in vacuo, with about 140° less of heat, than are required under a mean pressure of the atmospheret. Even the ordinary variations in the weight of the air, as measured by the barometer, are sufficient to make a difference in the boiling point of water of about 5° between the two extremest. (In ascending considerable heights, as to the tops of mountains, the boiling point of water gradually falls on the scale of the thermometer. Thus on the summit of Mount Blanc, water was found by Saussure to boil at 187° Fahrenheit. On this fact is founded the use of the thermometer in the measurement of heights, which though originally suggested by Fah-

<sup>\*</sup> Ann. de Chim. et Phys. vii. 307, or Journ. of Science, v. 361.

<sup>†</sup> Black's Lectures, i. 151.

<sup>‡</sup> Sir G. Shuckburgh, in Philosophical Transactions, lxxix. 375, and Gen. Roy in ditto, lxvii. 687.

<sup>§</sup> Phil. Trans. 1817, p. 184. The instrument is sold by Mr. Carey in the. Strand.

renheit, has only lately been made conveniently practicable, in consequence of the invention of a thermometer, adapted to the purpose, by the Rev. Mr. Wollaston\*. Without entering into minute details, it would not be possible to give a clear idea of the instrument. It may be sufficient to state that each degree about the boiling point is made to occupy a space, that admits of being distinctly divided into 1000 parts. And as each degree of Fahrenheit is equivalent to 530 feet, it follows that one thousandth part of a degree will be equivalent to a difference in height of about six inches. In fact, the height of a common table produces a manifest difference in the boiling point of water, as ascertained by this sensible instrument.

The influence of a diminished pressure in facilitating ebullition may, also, be illustrated by the following very simple experiment:—Place, over a lamp, a Florence flask, about three fourths filled with water; let it boil briskly during a few minutes; and, immediately on removing it from the lamp, cork it tightly, and suddenly invert it. The water will now cease to boil; but, on cooling the convex part of the flask by a stream of cold water, the boiling will be renewed. Applying boiling water from the spout of a tea-kettle to the same part of the flask, the water will again cease to boil. This renewal of the ebullition, by the application of cold (an apparent paradox) is owing to the formation of an imperfect vacuum over the hot water, by the condensation of steam; and the suspension of the boiling, on re-applying the heat, to the renewed pressure on the surface of the hot water, occasioned by the formation of fresh steam.

From these facts, it may be inferred, that the particles of caloric are mutually repulsive, and that they communicate this repulsive tendency to other bodies in which caloric is contained. This repulsive power tends to change solids into fluids, and liquids into aëriform bodies, and is chiefly counteracted by the pressure of the

atmosphere.

Were this counteracting cause removed, many bodies, which at present have a liquid form, would cease to be such, and would be changed into a gaseous state. Precisely the same effect, therefore, results from the prevalence of either of these forces. Add to certain liquids a quantity of caloric; in other words, place them in a high temperature, and they are immediately converted into gases: or, their temperature remaining the same, diminish the weight of the atmosphere; and the caloric, which they naturally contain, exerts its repulsive tendency with equal effect, and they are in like manner converted into gases. These facts are best shown by the following experiments on ether:

1. Ether, at the temperature of 104°, exists in the state of a gas. This may be shown by filling a jar with water of this temperature, and inverting it in a vessel of the same. Then introduce a little other, by means of a small glass tube closed at one end. The ether

<sup>\*</sup> Phil. Trans. 1817, p. 184. The instrument is sold by Mr. Carey in the Strand.

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will rise to the top of the jar, and, in its ascent, will be changed into gas, filling the whole jar with a transparent, invisible, elastic fluid. On permitting the water to cool, the ethereal gas is condensed, and

the inverted jar again becomes filled with water.

2. Ether is changed into gas by diminishing the weight of the atmosphere. Into a glass tube, about six inches long, and half an inch in diameter, put a tea-spoonful of ether, and fill up the tube with water; then, pressing the thumb on the open end of the tube, place it, inverted, in a jar of water. Let the whole be set under the receiver of an air pump, and the air exhausted. The ether will be changed into gas, which will expel the water entirely from the tube. On re-admitting the air into the receiver, the gas is again condensed into a liquid form.

IV. On the contrary, by considerably increasing the pressure, water may be heated to above 400° Fahrenheit, without being changed into vapour.—This experiment requires, for its performance, a strong iron vessel, called a Papin's digestor, a plate of which may be seen in Gren's Chemistry. That the boiling point of water, and the temperature of steam, are raised by an increased pressure, may be shown, however, by means of the small boiler, represented, plate v. fig. 46, which will be found extremely useful in experiments on this subject. Its precise size, and directions for its construction,

will be given in the Description of the Plates.

On the cock c may be screwed, occasionally, a valve, loaded in the proportion of 14 pounds to the square inch. The boiler being rather more than half filled with water, and the perforated cap d being screwed into its place, the ball of the thermometer will be an inch or more above the surface of the water, and will indicate its temperature, as well as that of the steam, both being, necessarily, in all cases, precisely the same. Allowing the steam to escape through the cock c, before affixing the valve, the temperature of the steam, under a mean atmospheric pressure, will be 212°. When an additional atmosphere is added by the weighted valve, it will rise to above 240°; by a valve twice as heavy as the first, or loaded in the proportion of 42 pounds to the square inch (= three atmospheres), the temperature of the steam will be raised to nearly 270°. as far as it is safe to carry the experiment; but by substituting a strong iron vessel, the numbers have been obtained, which will be found in the form of a table, in the Appendix.

V. The absorption of caloric, during evaporation, shown by experiment.—Moisten a thermometer with alcohol, or with ether, and expose it to the air, repeating these operations alternately. The mercury of the thermometer will sink at each exposure, because the volatile liquor, during the evaporation, robs it of its heat. In this way (especially with the aid of an apparatus described by Mr. Cavalle, in the Philosophical Transactions, 1781, p. 509), water may be frozen in a thin and small glass ball, by means of ether. The same effect may be obtained, also, by immersing a tube, containing water at the bottom, in a glass of ether, which is to be placed under the receiver of an air pump; or the ether may be allowed to float on

the surface of the water. During the exhaustion of the vessel, the ether will evaporate rapidly; and, robbing the water of heat, will completely freeze it; thus exhibiting the singular spectacle of two fluids in contact with each other, one of which is in the act of boiling,

and the other of freezing, at the same moment.

By a little modification of the experiment, mercury itself, which requires for congelation a temperature of almost 40° below 0 of Farenheit, may be frozen, as was first shown by Dr. Marcet\*. A conical receiver, open at the top, is placed on the plate of an air pump, and a mercurial thermometer is suspended within the receiver, through the aperture, by means of a brass plate, perforated in its centre, and fitting the receiver air tight, when laid upon its open The thermometer passes through this plate, to which it is fitted by a leather adjustment, or simply by a cork secured with sealing wax; and it is so graduated, that, when its bulb is sunk a few inches within the receiver, the stem rises externally through the plate, above which the scale begins. The bulb is then wrapped up, in a little cotton wool, or, what is better, in a small bag of fine fleecy hosiery; and, after being dipped into ether, the apparatus is quickly laid over the receiver, which is exhausted as rapidly as possible. In two or three minutes the temperature sinks to about 45° below 0, at which moment the quicksilver in the stem suddenly descends with great rapidity. If it be desired to exhibit the mercury in a solid state, common tubes may be used, which have originally been about an inch diameter, but have been flattened by pressure, when softened by the blow-pipe. The experiment succeeds, when the temperature of the room is as high as 40° Fahrenheit.

VI. The fixation of caloric in water, by its conversion into steam may be shown by the following experiments:—1. Let a pound of water at 212°, and eight pounds of iron filings at 300°, be suddenly mixed together. A large quantity of vapour will be instantly generated; and the temperature of the mixture will be only 212°; but that of the vapour produced is also not more than 212°; and the steam must therefore contain, in a latent or combined form, all the caloric which raised the temperature of eight pounds of iron filings

from 212° to 300°.

2. The quantity of caloric, which thus becomes latent during the formation of steam, may be approximated, by repeating the following experiment of Dr. Black: He placed two cylindrical flat-bottomed vessels of tin, five inches in diameter, and containing a small quantity of water at 50°, on a red hot iron plate, of the kind used in kitchens. In four minutes the water began to boil, and in twenty minutes the whole was boiled away. In four minutes, therefore, the water received  $162^{\circ}$  of temperature, or  $40^{\circ}$ , in each minute. If we suppose, therefore, that the heat continues to enter the water at the same rate, during the whole ebullition, we must conclude that  $401^{\circ} \times 20 = 810^{\circ}$  have entered the water, and are contained in the vapour.

It has been found by experiment that 75 pounds of Newcastle coal, or 100 pounds of coal of medium quality, applied in the best manner, are required for the vaporization of 12 cubic feet, or about 89\(\frac{3}{4}\) wine gallons, of water. A pound of coal, on the average, may be considered as equivalent to convert a gallon of water into vapour. Wood charcoal, by combustion, is capable of melting 94 times its weight of ice, and of evaporating 13 times its weight of water, previously at 32° Fahrenheit. Peat of the best quality, when properly applied, evaporates 10 times its weight of water, but, as commonly used, only 4 or 5 times. Even with the assistance of heated air, only six times its weight can be evaporated, though Cµraudau pretends to have evaporated 25 times its weight. From evidence given before the House of Commons on the Gas Light Bill 17\(\frac{1}{2}\) pounds of good London coke appear to be capable of raising from 66 to 70 pounds of water into vapour, or about 4 times their weightt.

VII. Water, by conversion into steam, has its bulk prodigiously enlarged, viz. according to Mr. Watt's experiments, about 1800 times, or, according to Gay Lussac, only 1698 times. A cubit inch of water (or 252 grains) occupies, therefore, when converted into steam, the space of about a cubit foot. Hence its specific gravity, under the ordinary pressure of the air is to that of common air, nearly as 450 to 1000; or, taking Gay Lussac's data, as 10 to 16, or 625 to 1000.

VIII. On the contrary, vapours, during their conversion into liquid form, evolve, or give out, much caloric.—The heat given out, by the condensation of steam, is rendered apparent by the following experiment: Mix 100 gallons of water at 50°, with 1 gallon of water at 212°. The temperature of the water will be raised about 1½°. Condense by a common still-tub, 1 gallon of water, from the state of steam, by 100 gallons of water, at the temperature of 50°. The water will be raised 11°. Hence, 1 gallon of water, condensed from steam, raises the temperature of 100 gallons of cold water 9½° more than 1 gallon of boiling water; and, by an easy calculation, it appears that the caloric imparted to the 100 gallons of cold water by 8 pounds of steam, if it could be condensed in 1 gallon of water, would raise it to 950°‡. The quantity of ice, which is melted by steam of ordinary density, is invariably 7½ times the weight of the steam.

For exhibiting the latent heat of steam, by means of a small apparatus, which may be placed on a table, and with the assistance only of a lamp, the boiler already described (fig. 46) will be found extremely well adapted. The right angled pipe e must be screwed, however, into its place, and must be made to terminate at the bottom of a jar, containing a known quantity of water of a given temperature. This conducting pipe and the jar should be wrapped round with a few folds of flannel. The apparatus being thus disposed, let

<sup>\* 79</sup> An. Ch. 86.

<sup>†</sup> See also Count Rumford's Researches on the Heat developed in Combustion. Phil. Mag. xli. xlii. and xliii. ‡ Black's Lectures, i. 169.

the water in the boiler be heated by an Argand's lamp, with double concentric wicks, till steam issues in considerable quantity through the cock c, which is then to be closed. The steam will now pass through the right angled pipe into the water contained in the jar, which will condense the steam, and will have its temperature very considerably raised. Ascertain the augmentation of temperature and weight; and the result will show, how much a given weight of water has had its temperature raised by a certain weight of condensed steam. To another quantity of water, equal in weight and temperature to that contained in the jar at the outset of the experiment, add a quantity of water at 212°, equal in weight to the condensed steam; it will be found, on comparison of the two resulting temperatures, that a given weight of steam has produced, by its condensation, a much greater elevation of temperature, than the same quantity of boiling water. This will be better understood by the following example, taken from actual experiment:

Into eight ounces of water, at 50° Fahrenheit, contained in the glass jar, f. fig. 46, steam was passed from the boiler, till the temperature of the water in the jar rose to 173°. On weighing the water, it was found to have gained 8½ drachms; that is, precisely 8½ drachms of steam had been condensed, and had imparted its heat to the water.—To facilitate the explanation of this experiment, it is

necessary to premise the following remarks.

To measure the whole quantities of caloric contained in different bodies, is a problem in chemistry which has not yet been solved. But the quantities of caloric, added to or subtracted from, different bodies (setting out from a given temperature) may, in many cases, be measured and compared with considerable accuracy. Thus, if, as has been already stated, two pounds of water at 120° be mixed with two pounds at 60°, half the excess of caloric in the hot water will pass to the colder portion; that is, the hot water will be cooled 30°, and the cold will receive 30° of temperature; and if the experiment be conducted with proper precautions, 90°, the arithmetical mean of the temperature of the separate parts, will be the temperature of the mixture. If three pounds of water at 100° be mixed with one pound at 60°, we shall have the same quantity of heat as before, viz. four pounds at 90°. Hence, if the quantity of water be multiplied by the temperature, the product will be a comparative measure of the quantity of caloric which the water contains, exceeding the zero of the thermometer employed.

# Thus, in the last example,

 $3 \times 100 = 300 =$  the caloric above zero in the first portion.  $1 \times 60 = 60 =$  the caloric above zero in the second do.

The sum, 360 = the caloric above zero in the mixture. Dividing 360 by 4, the whole quantity of water, we obtain 90°, the temperature of the mixture.

This method of computation may be conveniently applied to a variety of cases. Thus, in the foregoing experiment, 8½ drachms of steam at 212°, added to 64 drachms of water at 50°, produced 72½ drachms of water at 173°. Now,

Therefore 9342½ divided by 8½ = 1099, should have been the temperature of the latter portion (viz. 8½ drachms), had none of its heat been latent: and 1099 — 212 = 837 gives the latent heat of the steam. This result does not differ more than might be expected, owing to the unavoidable inaccuracies of the experiment, from Mr. Watt's determination, which states the latent heat of steam at 900°, or from that to 950°\*. Lavoisier, with the aid of the calorimeter, makes it 1000°, or a little more.

IX. The same weight of steam contains, whatever may be its density, the same quantity of caloric; its latent heat being increased in exact proportion as its sensible heat is diminished; and the reverse. This principle, though scarcely admitting of illustration by any easy experiment, is one of considerable importance; and an ignorance of it has been the occasion of many fruitless attempts to improve the economy of fuel in the steam engine. The fact, so far as respects steam of lower density than that of 30 inches of mercury, was long ago determined experimentally by Mr. Wattt. As the boiling point of liquids is known to be considerably reduced under a diminished pressure, it seemed reasonable to suspect that, under these circumstances, steam might be obtained from them with a less expenditure of heat. Water, Mr. Watt found, might easily be distilled in vacuo when at the temperature of only 70° Fahrenheit. But, by condensing steam formed at this temperature, and observing the quantity of heat which it communicated to a given weight of water, he determined that its latent heat, instead of being only 955°, was between 1200° and 1300°.

The same principle may be explained also by the following illustration, which was suggested to me by Mr. Ewart. Let us suppose that in a cylinder, furnished with a piston, we have a certain quantity of steam, and that it is suddenly compressed, by a stroke of the piston, into half its bulk. None of the steam will in this case be condensed; but it will acquire double elasticity, and its temperature will be considerably increased. Now if we either suppose the cylinder incapable of transmitting heat, or take the moment instantly following the compression before any heat has had time to escape, it must be evident that the sensible and latent heat of the steam, taken together before compression, are precisely equal to the sensi-

<sup>\*</sup> Black's Lectures, i. 174.

ble and latent heat taken together of the denser steam. But in the dense steam, the sensible heat is increased, and the latent heat proportionally diminished. The explanation of this fact will be furnished by a principle to be hereafter explained, that the capacities of clastic fluids for caloric are uniformly diminished by increasing their density.

X. The evaporation of water is carried on much more rapidly under a diminished pressure, especially if the vapour, which is formed, be condensed as soon as it is produced, so as to keep up the vacuum.

On this principle depends Mr. Leslie's new and ingenious mode of freezing water, in an atmosphere of medium temperature, by producing a rapid evaporation from the surface of the water itself. The water to be congealed is contained in a shallow vessel, which is supported above another vessel, containing a strong sulphuric acid, or dry muriate of lime; or even dried garden mould or parched oatmeal. Any substance, indeed, that powerfully attracts moisture, may be applied to this purpose. The whole is covered by the receiver of an air pump, which is rapidly exhausted; and as soon as this is effected, crystals of ice begin to shoot in the water, and a considerable quantity of air makes its escape, after which the whole of the water becomes solid. The rarefaction required is to about 100 times; but to support congelation, after it has taken place, 20 or even 10 times are sufficient. The sulphuric acid becomes very warm; and it is remarkable, that if the vacuum be kept up, the ice itself evaporates. In five or six days, ice of an inch in thickness will entirely disappear. The acid continues to act, till it has absorbed an equal volume of water.

An elegant manner of making the experiment is to cover the vessel of water with a plate of metal or glass, fixed to the end of a sliding wire, which must pass through the neck of the receiver, and be, at the same time, air tight, and capable of being drawn upwards. When the receiver is exhausted, the water will continue fluid, till the cover is removed, when, in less than five minutes, needle-shaped crystals of ice will shoot through it, and the whole will soon become frozen.

In this interesting process, if it were not for the sulphuric acid, an atmosphere of aqueous vapour would fill the receiver; and, pressing on the surface of the water, would prevent the further production of vapour. But the steam, which rises, being condensed the moment it is formed, the evaporation goes on very rapidly, and has no limits but the quantity of the water, and the diminished concentration of the acid\*.

It is on the same principle, that the instrument invented by Dr. Wollaston, and termed by him the *Cryophorus*, or *Frostbearer*, is founded. It may be formed by taking a glass tube, having an inter-

a salaman .... a ... Alberta

<sup>\*</sup> The most complete account of this new mode of freezing is to be found in the Supplement, now publishing, to the Encycl. Brit. art. Cold.

<sup>†</sup> See plate 10.

nal diameter of about 3th of an inch diameter, the tube being bent to a right angle at the distance of half an inch from each ball. One of these balls should be about half filled with water, and the other should be as perfect a vacuum as can readily be obtained, the mode of effecting which is well known to those accustomed to blow glass. One of the balls is made to terminate in a capillary tube; and when the water in the other ball has been boiled over a lamp a considerable time, till all the air is expelled, the capillary extremity, through which the steam is still issuing with violence, is held in the flame of the lamp, till the force of the vapour is so far reduced, that the heat of the flame has power to seal it hermetically.

When an instrument of this kind is well prepared, if the empty ball be immersed in a mixture of snow and salt, the water in the other ball, though at the distance of two or three feet, will be frozen solid in the course of a very few minutes. The vapour in the empty ball is condensed by the common operation of cold; and the vacuum produced by this condensation gives opportunity for a fresh quantity to arise from the opposite ball, with a proportional reduc-

tion of its temperature.

The large quantity of caloric, latent in steam, renders its application extremely useful for practical purposes. Thus, water may be heated, at a considerable distance from the source of heat, by lengthening the conducting pipe e, fig. 46. This furnishes us with a commodious method of warming the water of baths, which in certain cases of disease, it is of importance to have near the patient's bedroom; for the boiler, in which the water is heated, may thus be placed on the ground-floor, or in the cellar of a house; and the steam conveyed by pipes into an upper apartment. Steam may also be applied to the purpose of heating or evaporating water, by a modification of the apparatus. Fig. 46, g, represents the apparatus for boiling water by the condensation of steam, without adding to its quantity; a circumstance occasionally of considerable importance. The steam is received between the vessel, which contains the water to be heated, and an exterior case; it imparts its caloric to the water. through the substance of the vessel, is thus condensed, and returns to the boiler by the perpendicular pipe. An alteration of the form of the vessel adapts it to evaporation (fig. 46, h). This method of evaporation is admirably suited to the concentration of liquids, that are decomposed, or injured, by a higher temperature than that of boiling water, such as medicinal extracts; to the drying of precipitates, &c. In the employment of either of these vessels, it is expedient to surround it with some slow conductor of heat. On a small scale, a few folds of woollen cloth are sufficient; and, when the vessel is constructed of a large size for practical use, this purpose is served by the brick-work in which it is placed.

#### SECTION V.

### Specific Caloric.

Equal weights of the same body, at the same temperature, contain the same quantities of caloric. But equal weights of different bodies at the same temperature, contain unequal quantities of caloric. The quantity of caloric, which one body contains, compared with that contained in another, is called its specific caloric; and the power or property, which enables bodies to retain different quantities of caloric, has been called capacity for caloric. The method of determining the specific caloric, or comparative quantities of caloric in different bodies, is as follows:

It has already been observed, that equal weights of the same body, at different temperatures, give, on admixture, the arithmetical mean. Thus, the temperature of a pint of hot water and a pint of cold, is, after mixture, very nearly half way between that of the two extremes. But this is not the case, when equal quantities of different

bodies, at different temperatures, are employed.

(a) If a pint of quicksilver at 100° Fahrenheit, be mixed with a pint of water at 40°, the resulting temperature will not be 70° (the arithmetical mean), but only 60°. Here the quicksilver loses 40° of heat, which nevertheless raise the temperature of the water only 20°; in other words, a larger quantity of caloric is required to raise the temperature of a pint of water, than that of a pint of mercury, through the same number of degrees. Hence it is inferred, that water has a greater capacity for caloric than is inherent in quicksilver.

(b) The experiment may be reversed, by heating the water to a greater degree than the quicksilver. If the water be at 100°, and the mercury at 40°, the resulting temperature will be nearly 80°; because the pint of hot water contains more caloric, than is necessa-

ry to raise the quicksilver to the arithmetical mean.

(c) Lastly, if we take two measures of quicksilver to one of water, it is of no consequence which is the hotter; for the resulting temperature is always the mean between the two extremes; for example, 70°, if the extremes be 100° and 40°. Here, it is manifest, that the same quantity of caloric, which makes one measure of water warmer by 30°, is sufficient for making two measures of quicksilver warmer by the same number. Quicksilver has, therefore, a less capacity than water for caloric, in the proportion, when equal measures are taken, of one to two.

If, instead of equal bulks of quicksilver and water, we had taken equal weights, the disparity between the specific caloric of the mercury and water would have been still greater. Thus a pound of water at 100°, mixed with a pound of mercury at 40°, gives a temperature of  $97\frac{1}{2}$ °, or  $27\frac{1}{2}$ ° above the arithmetical mean. In this experiment, the water, being cooled from 100° to  $97\frac{1}{2}$ ° has lost a quantity of caloric reducing its temperature only  $2\frac{1}{2}$ °; but this caloric, communicated to the pound of mercury, has produced in its temperature

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a rise of no less than  $57\frac{1}{2}^{\circ}$ . Therefore, a quantity of caloric, necessary to raise the temperature of a pound of water  $2\frac{1}{2}^{\circ}$ , is sufficient to raise that of a pound of mercury  $57\frac{1}{2}^{\circ}$ ; or by the rule of proportion, the caloric which raises the temperature of a pound of water 1°, will raise that of a pound of quicksilver about 23°. Hence it is inferred, that the quantity of caloric contained in water, is to that contained in the same weight of quicksilver as 23° to 1°. Or, stating the calloric of water at 1°, that of quicksilver will be  $\frac{1}{23}$  part of 1°, or 0,0435\*.

When this comparison is extended to a great variety of bodies, they will be found to differ very considerably in their capacities for caloric. The results of numerous experiments of this kind are com-

prised in a table of specific caloric t.

The capacities of bodies for caloric influence, considerably, the rate at which they are heated and cooled. In general, those bodies are most slowly heated, and cool most slowly, which have the greatest capacities for heat ‡. Thus if water and quicksilver be set, in similar quantities and at equal distances before the fire, the quicksilver will be much more rapidly heated than the water; and, on removal from the fire, it will cool with proportionally greater quickness than the water. By ascertaining the comparative rates of cooling, we may even determine, with tolerable exactness, the specific caloric of bodies; and particularly of one class (the gases), which are not easily compared in any other ways. The specific heat of the different aëriform fluids will be stated, on the authority of Delaroche and Berard, in the chapter on gases.

#### CHAPTER IV.

#### OF LIGHT.

THE laws of light, so far as they relate to the phenomena of its movement, and to the sense of vision, constitute the science of ortics; and therefore, not of Chemistry, but of Natural Philosophy. Light, however, is capable of producing important chemical effects, and of entering into various chemical combinations. Its action is, for the most part, exerted in de-oxidizing bodies; the facts of this kind cannot be perfectly understood, until two important classes of bodies have been described, viz. those of oxides and of acids. In this place

The above numbers, which differ from those commonly stated, are given on the authority of Mr. Dalton.

<sup>†</sup> See the Appendix.

<sup>#</sup> See Martine, on Heat, page 74.

<sup>§</sup> See Leslie on Heat, chap. xxi. and Despretz Ann. de Chim. et Physvi. 184.

therefore, I shall state only a few of its least complicated effects; and shall trace its agency on different bodies, as they become the ob-

jects of experiment in the sequel.

I. Light, in the state in which it reaches the organ of vision, it is well known, is not a simple body, but is capable of being divided, by the prism, into seven primary rays or colours, viz. red, orange, yellow, green, blue, and violet. These are refrangible in the above order, the red being least refrangible, and the voilet most so. The image formed by the different rays thus separated, constitutes the solar spectrum. If it be divided into 300 parts, the red will occupy 45 of these parts, the orange 27, the yellow 48, the green 60,

the indigo 40, and the violet 80.

II. Heat and light are not present, in corresponding degrees, in different parts of the solar spectrum. With respect to the illuminating power of each colour, Dr. Herschell found that the red rays are far from having it in an eminent degree. The orange possess more of it than the red; and the yellow rays illuminate objects still more perfectly. The maximum of illumination lies in the brightest yellow or palest green. The green itself is nearly equally bright with the yellow; but from the full deep green, the illuminating power decreases very sensibly. That of the blue is nearly on a par with that of the red; the indigo has much less than the blue, and the violet is very deficient\*.

III. The heating power of the rays follow a different order.

—If the bulb of a very sensible air thermometer be moved in succession, through the differently coloured rays, it will be found to indicate the greatest heat in the rays; next in the green; and so on in a diminishing progression, to the violet. The precise effects of the different rays, determined by Dr. Herschell's experiments, are as follow:

## The thermometer rose

•						
In the blue	in	3	minutes from	55°	to	560
green,	in	3		54	to	58
yellow,	in	3		56	to	62
full red,	in	2	<u> </u>	56	to	72
confines of red	, in	2	<del></del>	58	to	73½

IV. When the thermometer is removed entirely out of the confines of the red rays, but with its ball still in the line of the spectrum, it rises even higher than in the red rays; and continues to rise, till removed half an inch beyond the extremity of the red rays. In this situation, quite out of the visible light, the thermometer rose in 2½ minutes from 61 to 79. The ball of the thermometer, employed for this purpose, should be extremely smallt, and should be blackened with Indian ink. An air thermometer is better adapted than a mercurial one, to exhibit the minute change of temperature that en-

<sup>\*</sup> Philosophical Transactions, 1800, page 267.

<sup>†</sup> Excellent thermometers for this purpose, and others requiring great sensibility, are made by Mr. Crichton, of Glasgow, and Mr. Carey, of London.

sues. These invisible heat-making rays may be reflected by the mirror, and refracted by the leus, exactly in the same manner as the

rays of light.

A fact has been ascertained by Dr. Delaroche, which seems to point out a close connection between heat and light, and a gradual passage of the one into the other. The rays of invisible heat pass through glass with difficulty, at a temperature below that of boiling water; but they traverse it with a facility always increasing with the temperature, as it approaches the point when bodies become luminous. From these experiments, it would appear that the modification, whatever it be, which must be impressed on the invisible rays, to render them capable of penetrating through glass, makes them approach more and more to the state in which they must be, when they enter the eye, and occasion the sensation of vision.

The experiments of Dr. Herschell, already confirmed by sir H. Englefield and other philosophers, were found correct in the main, when repeated by Mr. Berard\*, the same progressive heating power being observed in the rays from the violet to the red. But he found the greatest heating power at the extremity of the spectrum, and not beyond it. He fixed it at the point, where the bulb of the thermometer was still entirely covered by the red ray; and the thermometer sunk progressively, in proportion as the distance of its bulb from the red ray increased. Entirely out of the visible spectrum, where Herschell fixed the maximum of heat, its elevation above the ambient air was only one fifth of what it had been in the red ray itself. The reflection of invisible radiant heat, Mr. Berard-

found, follows precisely the same law as that of light.

V. Beyond the confines of the spectrum on the other side, viz.a little beyond the violet ray, the thermometer is not affected; but in this place it is remarkable, that there are also invisible rays of a different kind, which exert all the chemical effects of the rays of light, and with even greater energy. One of the chemical properties of light, it will hereafter be stated, is, that it speedily changes, from white to black, the fresh-precipitated muriate of silvert. This effect is produced most rapidly by the direct light of the sun; and the rays, as separated by the prism, have this property in various degrees. The blue rays, for example, effect a change of the muriate of silver in 15 seconds, which the red require 20 minutes to accomplish; and, generally speaking, the power diminishes as we recede from the violet extremity. But entirely out of the spectrum, and beyond the violet rays, the effect is still produced. Hence it appears, that the solar beams consist of three distinct kinds of rays: of those that excite heat, and promote oxidation; of illuminating rays; and of DE-OXIdizing or hydrogenating rays. It has lately, also, been asserted by Morrichini, that the violet rays have a magnetising power, and are capable of reversing the poles of a needle already magnetict.

<sup>\*</sup> Thomson's Annals, ii. 163. † See chap. xviii, sect. iv. ‡ Ann. de Chim. et Phys. jii. 323; Jour. of Science, v. 138; and Thomson's Annals, xii. 1.

A striking illustration of the different power of the various kinds of rays is furnished, by their effect on phosphorus. In the rays beyond the red extremity, phosphorus is heated, smokes, and emits white fumes; but these are presently suppressed, on exposing it to the

de-oxidizing rays, which lie beyond the violet extremity.

"I found," says Sir H. Davy\*, "that a mixture of chlorine and hydrogen acted more rapidly upon each other, combining without explosion, when exposed to the red rays, than placed in the violet rays; but that solution of chlorine in water became solution of muriatic acid most rapidly, when placed in the most refrangible rays of the spectrum. Puce-coloured oxide of lead, when moistened, gradually gained a tint of red in the least refrangible rays, and at last became black, but was not affected in the most refrangible rays; and the same change was produced by exposing it to a current of hydrogen gas. The oxide of mercury, procured by a solution of potash and calomel, exposed to the spectrum, was not changed in the most refrangible rays, but became red in the least refrangible ones, which must have depended on its absorbing oxygen. The violet rays produced, upon moistened red oxide of mercury, the same effects as hydrogen gas."

The experiments of Berardt confirm those of Ritter and Wollaston. To show the disproportion between the energies of the different rays, he concentrated, by means of a lens, all that part of the spectrum, which extends from the green to the extreme violet; and, by another lens, all that portion, which extends from the green to the extremity of the red. In the focus of this last, though intensely bright to the eyes, muriate of silver remained above two hours unaltered; but in that of the former, though much less bright, it was

blackened in less than six minutes.

VI. There is an exception however, as stated by Dr. Wollaston, to the de-oxidizing power of the rays above-mentioned. The substance, termed gum-guaiacum, has the property, when exposed to the light, of being changed from a yellowish colour to green; and this effect he has ascertained to be connected with the absorption of oxygen. Now in the most refrangible rays, which would fall beyond the violet extremity, he found that this substance became green, and was again changed to yellow by the least refrangible. This is precisely the reverse of what happens to muriate of silver, which is blackened, or de-oxidized, by the most refrangible; and has its colour restored, or is again oxygenized, in the least refrangible rays.

lour restored, or is again oxygenized, in the least refrangible rays. VII. Certain bodies have the property of absorbing the rays of light in their totality; of retaining them for some time; and of again evolving them unchanged, and unaccompanied by sensible heat. Thus, in an experiment of Du Fay, a diamond exposed to the sun, and immediately covered with black wax, shone in the dark, on removing the wax, at the expiration of several months. Bodies, gifted with this property, are called SOLAR PHOSPHORI. Such are Canton's, Baldwin's, Homberg's, and the Bolognian phosphori, which

<sup>\*</sup> El. of Chim. Phil. p. 211.

will be described hereafter. To the same class belong several natural bodies, which retain light, and give it out unchanged. Thus snow is a natural solar phosphorus. So also is, occasionally, the sea when agitated; putrid fish have a similar property; and the glow-worm belongs to the same class. These phenomena are independent of every thing like combustion; for artificial phosphori, after exposure to the sun's rays, shine in the dark, when placed in the vacuum of an air-pump, or under water, &c. where no air is present to effect combusiton.

VIII. From solar phosphori, the extrication of light is facilitated by the application of an elevated temperature; and, after having ceased to shine at the ordinary temperature, they again emit light when exposed to an increase of heat. Several bodies, which do not otherwise give out light, evolve it, or become phosphorescent, when Thus, powdered fluate of lime becomes luminous, when thrown on an iron plate raised to a temperature rather above that of boiling water; and one of its varieties, known to mineralogists under the name of chlorophane, gives out abundantly an emerald green light by the mere heat of the hand; and after being exposed to the sun, or even to a candle, continues to shine in a dark place for some time\*. The yolk of an egg, when dried, becomes luminous, on being heated; and so also does tallow during liquefaction. To exhibit the last mentioned fact, it is merely necessary to place a lump of tallow on a coal, heated below ignition, making the experiment in a dark room.

IX. Attrition, also, evolves light. Thus, two pieces of common bonnet cane, rubbed strongly against each other in the dark, emit a faint light. Two pieces of borax have the same property much more

remarkably.

X. Light is disengaged in various cases of chemical combination. Whenever combustion is a part of the phenomena, this is well known to happen; but light is evolved, also, in other instances, where nothing like combustion goes forward. Thus, fresh prepared pure magnesia, added suddenly to highly concentrated sulphuric

acid, exhibits a red heat.

XI. For measuring the relative intensities of light from various sources, an instrument has been contrived, called the photometer. That of Count Rumford, described in the 84th volume of the Philosophical Transactions, being founded on optical principles, does not fall strictly within the province of this work. It is constructed on the principle, that the power of a burning body, to illuminate any defined space, is directly as the intensity of the light, and inversely as the square of the distance. If two unequal lights shine on the same surface at equal obliquities, and an opaque body be interposed between each of them and the illuminated surface, the two shadows must differ in intensity or blackness; for the shadow formed by intercepting the greater light will be illuminated by the lesser light only; and, reversely, the other shadow will be illuminated by the

<sup>\*</sup> Thomson's Annals, ix. 17.

greater light; that is, the stronger light will be attended with the deeper shadow. But it is easy, by removing the stronger light to a greater distance, to render the shadow, which it produces, not deeper than that of the smaller, or of precisely the same intensity. This equalization being effected, the quantity of light emitted by each lamp, or candle, will be as the square of the distance of the burning

body from the white surface.

The photometer of Mr. Leslie is founded on a different principle, viz. that light, in proportion to its absorption, produces heat. The degree of heat produced, and consequently of light absorbed, is measured by the expansion of a confined portion of air. A minute description of the ingenious instrument contrived by Mr. Leslie with this view, may be seen in his work on Heat, or in the 3d vol. of Nicholson's 4to. Journal. In its construction, it bears a considerable resemblance to the differential thermometer, already described, page 75, and represented plate i. fig. 7. As both the balls of the latter instrument, however, are transparent, no change ensues in the situation of the coloured liquid when it is exposed to the variations of But, in the photometer, one of the balls is rendered opaque, either by tinging the glass, or by covering it with a pigment; and hence this ball, absorbing the incident light which passes freely through the transparent one, the air included in it becomes warnier than that of the other ball, and, by its great elasticity, forces the liquid up the opposite leg of the instrument. A graduated scale measures the amount of the effect; and a glass covering defends the photometer from being influenced by the temperature of the atmosphere.

The important discoveries of Malus, respecting the polarisation of light, scarcely fall within the province of this work, and I refer, therefore, for a popular statement of them to the 33d vol. of Nichol-

son's Journal, p. 344.

### CHAPTER V.

OF GASES.

#### SECTION I.

# Of the Apparatus for Gases.

For performing the necessary experiments on gases, many articles of apparatus are essential, that have not hitherto been described. It may assist the student in obtaining the necessary instruments, if a few of the most essential be here enumerated. In this place, however, I shall mention such only, as are necessary in making a few general experiments on this interesting class of bodies.

The apparatus, required for experiments on gases, consists partly of vessels fitted for containing the materials that afford them, and partly of vessels adapted for the reception of gases, and for submit-

ting them to experiment.

1. For procuring such gases as are producible without a very strong heat, glass bottles, furnished with ground stoppers and bent tubes, are sufficient (plate ii. fig. 18). Of these several will be required, of different sizes and shapes, adapted to different purposes. If these cannot be procured, a Florence flask, with a cork perforated, by a bent glass tube, or even by a tin pipe, will serve for obtaining some of the gases.

Those gases that require, for their liberation, a red heat, may be procured, by exposing to heat the substance capable of affording them, in earthern retorts or tubes; or in a gun barrel, the touchhole of which has been accurately closed by an iron pin. To the mouth of the barrel must be affixed a glass tube, bent so as to con-

vey the gases where it may be requisite.

A very convenient apparatus, for obtaining such gases as cannot be disengaged without a red heat, is sold at the shops for philosophical apparatus in London. It consists of a cast-iron retort, having a jointed metallic conducting tube fitted to it by grinding; by means of which the gas may be conveyed in any direction, and to any moderate distance. It is represented as placed, when in actual use, between the bars of a common fire-grate (plate ix. fig. 85, a, b.)

2. For receiving the gases, glass jars, of various sizes (figs. 21, 22, 23), are required, some of which should be furnished with necks at the top, fitted with ground stoppers. Others should be provided with brass caps, and screws, for the reception of air-cocks (fig. 22). Of these last (the air-cocks), several will be found necessary; and, to some of them, bladders, or elastic bottles, should be firmly tied, for the purpose of transferring gases. These jars will also be found extremely useful in experiments on the properties and effects of the gases. Some of them should be graduated into cubical inches.

To contain these jars, when in use, a vessel will be necessary, capable of holding a few gallons of water. This may either be of wood, if of considerable size; or, if small, of tin, japanned or painted. Plate iv. fig. 41, f f exhibits a section of this apparatus, which has been termed the pneumato-chemical trough, or pneumatic cistern. Its size may vary with that of the jars employed; and, about two or three inches from the top, it should have a shelf, on which the jars may be placed, when filled with air, without the risk of being overset. In this shelf should be a few small holes, to which inverted funnels may be soldered.

A glass tube, about 18 inches long, and three quarters of an inch diameter (fig. 24,) closed at one end, and divided into cubic inches, and tenths of inches, will be required for ascertaining the purity of air by nitrous gas. It should be accompanied also with a small measure, containing about two cubic inches, and similarly graduated. For employing the solution of nitrous gas in liquid sulphate of iron,

glass tubes, about five inches long, and half an inch wide, divided decimally, are also necessary. Besides these, the experimentalist should be furnished with air funnels, (fig. 19,) for transferring

gases from wide to narrow vessels.

An apparatus, almost indispensable in experiments on this class of bodies, is a GAZOMETER, which enables the chemist to collect and to preserve large quantities of gas, with the aid of only a few pounds of water. In the form of this apparatus there is considerable variety; but, at present, I have no other view than that of explaining its general construction and use. It consists of an outer fixed vessel d (plate iv. fig. 35), and an inner moveable one c, both of japanned iron. The latter slides easily up and down within the other, and is suspended by cords passing over pulleys, to which are attached the To avoid the encumbrance of a great weight of counterpoise, ee. water, the outer vessel d is made double, or is composed of two cylinders, the inner one of which is closed at the top and at the bot-The space of only about half an inch is left between the two cylinders, as shown by the dotted lines. In this space the vessel c may move freely up and down. The interval is filled with water as high as the top of the inner cylinder. The cup, or rim, at the top of the outer vessel, is to prevent the water from overflowing, when the vessel c is forcibly pressed down, in which situation it is placed whenever gas is about to be collected. The gas enters from the vessel in which it is produced, by the communicating pipe b, and passes along the perpendicular pipe marked by dotted lines in the centre, into the cavity of the vessel c, which continues rising till it is full.

To transfer the gas, or to apply it to any purpose, the cock b is to be shut, and an empty bladder, or bottle of clastic gum, furnished with a stop cock, to be screwed on a. When the vessel c is pressed down with the hand, the gas passes down the central pipe, which it had before ascended, and its escape at b being prevented, it finds its way up a pipe which is fixed to the outer surface of the vessel, and which is terminated by the cock a. By means of an ivory mouthpiece screwed upon this cock, the gas, included in the instrument, may be repaired; the nostrils being closed by the fingers. When it is required to transfer the gas into glass jars standing inverted in water, a crooked tube may be employed, one end of which is screwed upon the cock b; while the other aperture is brought under the inverted funnel, fixed into the shelf of the pneumatic trough. (See fig. 41, c.)

Several alterations have been made in the form of this apparatus; but they are principally such as add merely to its neatness and beauty, and not to its utility; and they render it less easy of explanation. The counterpoises ee are now, generally, concealed in the

framing, and the vessel c is frequently made of glass.

When large quantities of gas are required (as at a public lecture), the gas-holder, (plate iv. fig. 36), will be found extremely useful. It is made of tinned iron plate, japanned both within and without. Two short pipes, a and c, terminated by cocks, proceed from its Vol. I—P

sides, and another, b, passes through the middle of the top or cover, to which it is soldered, and reaches within half an inch of the bottom. It will be found convenient also to have an air-cock, with a very wide bore, fixed to the funnel at b. When gas is to be transferred into this vessel from the gazometer, the vessel is first completely filled with water through the funnel, the cock a being left open, and c shut. By means of a horizontal pipe, the aperture a is connected with a of the gazometer. The cock b being shut, a and care open, and the vessel c of the gazometer (fig. 35), gently pressed downwards with the hand. The gas then descends from the gazo-meter till the air-holder is full, which may be known by the water ceasing to escape, through the cock c. All the cocks are then to be shut, and the vessels disunited. To apply this gas to any purpose, an empty bladder may be screwed on a; and water being poured through the funnel b, a corresponding quantity of gas is forced into the bladder. By lengthening the pipe b, the pressure of a column of water may be added: and the gas being forced through a with considerable velocity, may be applied to the purpose of a blow-pipe, &c. &c. The apparatus admits of a variety of modifications. The most useful one appears to me to be that contrived by Mr. Pepys, consisting chiefly in the addition of a shallow cistern (e, plate ix. fig. 85) to the top of the air-holder, and of a glass register tube f, which shows the height of the water, and consequently the quantity of gas, in the vessel. A more minute account of it will be given in the description of the ninth plate\*.

The gazometer, already described, is fitted only for the reception of gases that are confineable by water; because quicksilver would act on the tinning and solder of the vessel, and would not only be spoiled itself, but would destroy the apparatus. Yet an instrument of this kind, in which mercury can be employed, is peculiarly desirable, on account of the great weight of that fluid; and two varieties of the mercurial gazometer have therefore been invented. The one, of glass, is the contrivance of Mr. Clayfield, and may be seen represented in the plate prefixed to Sir H. Davy's Researches. In the other, invented by Mr. Pepys, the cistern for the mercury is of castiron. A drawing and description of it may be found in the 5th vol. of the Philosophical Magazine; but as neither of these instruments are essential to the chemical student, and as they are required only in experiments of research, I deem it sufficient to refer to the minute descriptions of their respective inventors. Mr. Newman has lately joined a gazometer of this kind to an improved mercurial trough, by means of which the advantages of both are obtained with only 60 or 70 pounds of quicksilver. A description and drawing of this apparatus is given in the Journal of Science and the Arts, i. 186.

For those gases that are absorbed by water, a mercurial trough is necessary. For the mere exhibition of a few experiments on these condensible gases, a small wooden trough, 11 inches long, two wide,

<sup>\*</sup> Descriptions and figures of improved gas-holders may be seen also in the 13th, 24th, 27th, and 44th vols. of the Philosophical Magazine.

and two deep, cut out of a solid block of mahogany, is sufficient; but for experiments of research, one of considerable size is required.

(See plate iii. fig. 31, f. f.)

The apparatus, required for submitting gases to the action of electricity, is shown in plate ix. fig. 84; where a represents the knob of the prime conductor of an electrical machine; b a Leyden jar, the ball of which is in contact with it, as when in the act of charging; and c the tube standing inverted in mercury, and partly filled with gas. The mercury is contained in a strong wooden box d, to which is screwed the upright iron pillar e, with a sliding collar for securing the tube c in a perpendicular position. When the jar b is charged to a certain intensity, it discharges itself between the knob a and the small ball i, which, with the wire connected with it, may be occasionally fitted on the top of the tube c. The strength of the shocks is regulated by the distance between a and i.

By the same apparatus, inflammable mixtures of gases may be exploded by electricity. In this case, however, the jar b is unnecessary, a spark received by i from a being sufficient to kindle the mixture.

The method of weighing gases is very simple, and easily practised. For this purpose, however, it is necessary to be provided with a good air-pump; and with a globe or flask, furnished with a brass cap and air-cock, as shown fig. 22, b. A graduated receiver is also required, to which an air-cock is adapted, as shown at fig. 22, a.

Supposing the receiver a to be filled with any gas, the weight of which is to be ascertained, we screw the cock of the vessel b on the transfer plate of an air-pump, and exhaust it as completely as possible. The weight of the exhausted vessel is then very accurately taken, even to a small fraction of a grain; and it is screwed upon the air-cock of the receiver a. On opening both cocks, the last of which should be turned very gradually, the gas ascends from the vessel a; and the quantity, which enters into the flask, is known by the graduated scale on a. On weighing the vessel a second time, we ascertain how many grains have been admitted. If we have operated on common air, we shall find its weight to be at the rate of about 30.5 grains to 100 cubical inches. The same quantity of oxygen gas will weigh about 34 grains, and of carbonic acid gas upwards of 47 grains.

In experiments of this kind it is necessary either to operate with the barometer at 30 inches, and the thermometer at 60° Fahrenheit, or to reduce the volume of gas employed to that pressure and temperature, by rules which are given in the Appendix. Great care is to be taken, also, not to warm any of the vessels by contact with the hands, from which they should be defended by a glove. On opening the communication between the receiver and the exhausted globe, if any water be lodged in the air cock attached to the former, it will be forcibly driven into the globe, and the experiment will be frustrated. This may be avoided by using great care in filling the receiver with

water, before passing into it the gas under examination.

The specific gravity of any gas compared with common air is readily known, when we have once determined its absolute weight.

Thus if 100 cubic inches of air weigh 30.5 grains, and the same quantity of oxygen gas weighs 34 grains, we say,

30.5 : 34 :: 1.000 : 1.1147.

The specific gravity of oxygen gas will therefore be as 1.1147 to 1.000. We may determine, also, the specific gravity of gases, more simply, by weighing the flask, first when full of common air, and again when exhausted; and afterwards by admitting into it as much of the gas under examination as it will receive; and weighing it a third time. Now as the loss between the first and second weighing is to the gain of weight on admitting the gas, so is common air to the gas whose specific gravity we are estimating. Supposing for example, that by exhausting the flask it loses 30.5 grains, and that by admitting carbonic acid it gains 47; then

30.5:47::1.000 1.5409.

The specific gravity of carbonic acid is therefore 1.5409, air being taken at 1.000. And knowing its specific gravity, we can, without any farther experiment, determine the weight of 100 cubic inches of carbonic acid; for as the specific gravity of air is to that of carbonic acid, so is 30.5 to the number required; or

1.000: 1.5409:: 30.5: 47.

One hundred inches of carbonic acid, therefore, will weigh 47

grains.

Previously to undertaking experiments on other gases, it may be well for an unpractised experimentalist to accustom himself to the dexterous management of gases, by transferring common air from one vessel to others of different sizes.

1. When a glass jar, closed at one end, is filled with water, and held with its mouth downwards, in however small a quantity of water, the fluid is retained in its place by the pressure of the atmosphere on the surface of the exterior water. Fill in this manner, and invert, on the shelf of the pneumatic trough, one of the jars, which is furnished with a stopper (fig. 23). The water will remain in the jar so long as the stopper is closed; but immediately on removing it, the water will descend to the same level within as without: for it is now pressed, equally upwards and downwards, by the atmosphere, and falls therefore in consequence of its own gravity.

2. Place the jar, filled with water and inverted, over one of the funnels of the shelf of the pneumatic trough. Then take another jar, filled (as it will be of course) with atmospherical air. Place the latter with its mouth on the surface of the water: and on passing it in the same position below the surface, the included air will remain in its situation. Bring the mouth of the jar beneath the funnel in the shelf, and incline it gradually. The air will now rise in bubbles, through the funnel, into the upper jar, and will expel the water from

it into the trough.

3. Let one of the jars, provided with a stop-cock at the top be placed full of air on the shelf of the trough. Screw upon it an empty bladder; open the communication between the jar and the bladder, and press the former into the water. The air will then pass into the bladder, till it is filled; and when the bladder is re-

moved from the jar, and a pipe screwed upon it, the air may be again

transferred into a jar inverted in water.

4. For the purpose of transferring gases from a wide vessel standing over water, into a small tube filled with and inverted over mercury, I have long used the following contrivance of Mr. Cavendish. A tube, eight or ten inches long, and of very small diameter, is drawn out to a fine bore, and bent at this end, so as to resemble the italic letter l. The point is then immersed in quicksilver, which is drawn into the tube till it is filled, by the action of the mouth. Placing the finger over the aperture at the straight end, the tube, filled with quicksilver, is next conveyed through the water, with the bent end uppermost, into an inverted jar of gas. When the finger is removed, the quicksilver falls from the tube into the trough, or into a cup placed to receive it, and the tube is filled with the gas. whole of the quicksilver, however, must not be allowed to escape; but a column must be left, three or four inches long, and must be kept in its place by the finger. Remove the tube from the water; let an assistant dry it with blotting paper; and introduce the point of the bent end into the aperture of the tube standing over quicksilver. On withdrawing the finger from that aperture which is now uppermost, the pressure of the column of quicksilver, added to the weight of the atmosphere, will force the gas from the bent tube into the one standing in the mercurial trough.

On every occasion, when it is necessary to observe the precise quantity of gas, at the commencement and close of an experiment, it is essential that the barometer and thermometer should exactly correspond at both periods. An increased temperature, or a fall of the barometer, augments the apparent quantity of gas; and a reduced temperature or a higher barometer diminishes its bulk. Another circumstance, an attention to which is indispensable in all accurate experiments, is that the surface of the fluid, by which the gas is confined, should be precisely at the same level within and without the jar. If the fluid be higher within the jar, the contained gas will be under a less pressure than that of the atmosphere, the weight of which is counterpoised by that of the column of fluid within. In mercury, this source of error is of very considerable amount; as any person may be satisfied by pressing down, into quicksilver, a tube partly filled with that fluid, and partly with air, for the volume of the air will gradually decrease, the deeper the tube is immersed.

In experiments on gases, it is not always possible, however, to begin and conclude an experiment at precisely the same temperature, or with the same height of the barometer; or even to bring the mercury within and without the receiver to the same level. In these cases, therefore, calculation becomes necessary; and with the view of comparing results more readily and accurately, it is usual to reduce quantities of gas to the bulk they would occupy under one given pressure, and at a given temperature. In this country, it is now customary to assume as a standard 30 inches of the barometer, and 60° of Fahrenheit's thermometer; and to bring, to these standards, observations made under other degrees of atmospheric pressure

and temperature. The rules for these corrections, which are suffi-

ciently simple, I shall give in the Appendix.

Of experiments illustrative of the nature of gases in general, it may be proper to mention one or two that show the mode in which caloric exists in this class of bodies. In vapours, strictly so called, as the steam of water, caloric seems to be retained with but little force; for it quits the water when the vapour is merely exposed to a lower temperature. But, in gases, caloric is united by a very forcible affinity, and no diminution of temperature, that has ever vet been effected, can separate it from some of them. Thus the air of our atmosphere, in the most intense artificial or natural cold, still remains in the aëriform state. Hence is derived one character of gases, viz. that they remain aëriform under almost all variations of pressure and temperature; and in this class are also included those aërial bodies, which, being condensed by water, require confinement over mercury. The following experiment will show, that the caloric, contained in gases, is chemically combined.

Into a small retort (plate ii. fig. 26, b) put an ounce or two of well dried common salt, and about half its weight of sulphuric acid. By this process, a great quantity of gas is produced, which might be received and collected over mercury. But, to serve the purpose of this experiment, let it pass through a glass balloon, c, having three openings, into one of which the neck of the retort passes, while, from the other, a tube e proceeds, which ends in a vessel of water, f, of the temperature of the atmosphere. Before closing the apparatus, let a thermometer, d, be included in the balloon, to show the temperature of the gas. It will be found that the mercury, in this thermometer, will rise only a few degrees, whereas the water, in the vessel which receives the bent tube, will soon become boiling hot. In this instance, caloric flows from the lamp to the muriatic acid, and converts it into gas; but the heat, thus expended, is not appreciable by the thermometer. The caloric, however, is again evolved, when the gas is condensed by water. In this experiment, we trace caloric into a latent state, and again into the state of free or uncombined caloric.

A considerable part of the caloric, which exists in gases in a latent state, may be rendered sensible by rapid mechanical compression. Thus if air be suddenly compressed in the ball of an air-gun, the quantity of caloric liberated by the first stroke of the piston, is sufficient to set fire to a piece of the tinder called amadou\*. A flash of light is said, also, to be perceptible at the moment of condensation. This fact has been applied to the construction of a portable instrument for lighting a candle. It consists of a common syringe, concealed in a walking stick. At the lower extremity, the syringe is furnished with a cap, which receives the substance intended to be fired, and and which is attached to the instrument by a male and female screw. The rapid depression of the piston

<sup>\*</sup> Philosophical Magazine, xiv. 363, and xl. 424.

condenses the air, and evolves sufficient heat to set the tinder on fire\*.

For demonstrating the influence of variations of atmospheric pressure on the formation of gases, better experiments cannot be devised than those of Lavoisier. But as some students, who have the use of an air-pump, may not possess the apparatus described by Lavoisier (the glass bell and sliding wire), it may be proper to point out an easier mode of showing the same fact. This proof is furnished by the experiment already described, in which ether is made to assume alternately an aëriform and liquid state, by remov-

ing and restoring the pressure of the atmosphere.

Gases, when once formed, undergo a considerable change of bulk by variations of external pressure. The general law, which has been established on this subject is, that the volume of gases is inversely as the compressing force. If, for example, we have a quantity of gas occupying 60 cubic inches, under the common pressure of the atmosphere, it will fill the space of only 30 cubic inches, or one half, under a double pressure; of 20 inches, or one 3d, under a triple pressure; of 15 inches, or one 4th, under four times the pressure; and so on. When the pressure is sudden, considerable heat is evolved; and it appears, from Gay Lussac's experiments, that different gases, when equally compressed, give out different quantities of heat, bearing probably a proportion of their specific heats.

The law of the dilatibility of gases by heat has already been stated to be an enlargement of about 4 to the part of their bulk for each degree of Fahrenheit's scale, between the freezing and boiling points of water. At a temperature capable of rendering glass luminous (probably about 1035° Fahrenheit), 1 volume becomes about 2.5‡.

Before dismissing the consideration of the gases in general, there are a few properties, which it may be proper to notice, with the view of comparing the degree in which they belong to different in-

dividuals of the class.

I. The exact specific gravity of the different gases is a most important element, in calculating the proportion of the ingredients of compounds, into which they enter. Nothing, indeed, can show the importance of this object more strikingly, than the fact, that on the precise specific gravities of hydrogen and oxygen gases, depend the whole series of numbers, which are used to express the weights of the atoms of bodies on the Daltonian theory. The following Table exhibits the specific gravities of the most important of this class of bodies.

<sup>\*</sup> Philosophical Magazine, xxxi. 130.

<sup>†</sup> See his Elements, chap. 1. ‡ Davy, Phil. Trans. 1817. p. 54.

#### TABLE OF THE SPECIFIC GRAVITY OF GASES\*.

Barometer 30. Thermometer 60 °.

II. The determination of the specific heat of gases is a difficult and important problem, which has successively employed the labour and ingenuity of Crawford, Lavoisier and De la Place, Leslie, Gay Lussac, Dalton, and Delaroche and Berard. The results of the two last-mentioned philosophers, having been attained with the advantages of the improved state of the science, and of instruments of the greatest delicacy and refinement, are perhaps most entitled to confidence. The details of their experiments are given in the 85th volume of the Annales de Chimie, preceded by an historical review of the labours of their predecessors. The following Table contains the general results.

<sup>\*</sup> Gay Lussac's Table, which is more copious, but in which the numbers are not reduced to a mean of the barometer and thermometer, is copied into Thomson's Annals, ix. 16.; a Table by Professor Meinecke of Halle is inserted in the Journal of Science, &c. iii. 415.

#### TABLE OF THE SPECIFIC HEAT OF SOME GASES.

, N	AM	ES	QF	G,	SES						Under equal volumes.	Under equal weights.	Specific gravities.
Atmospheric a	ir		-	•	•		•	•	,		1.0000	1.0000	1.0000
Hydrogen gas											0.9033	12.340	0.0732
Oxygen gas.											0.9765	0.8848	1.1036
Nitrogen gas.								٠.			1.0000	1.0318	0.9691
Nitrous oxide									:		1.3503	0.8878	1.5209
Olefiant gas .	:	:	:	:	:	:	:	:	:	:	1.5530	1.5763	0.9885
Carbonic oxide	-	•	:	:	:	:	:	3	:	:	1.0340	1.0805	0.9569
Carbonic acid	į	:	:	:	:	:	;	:	:	:	1.2583	0.8280	1.5196

III. All solid bodies, that possess a certain degree of porosity, are capable of absorbing gases. This was first observed in charcoal, the power of which to condense different gases will be fully described in the section on that substance. It has been found, also, by Sausure, jun. to belong to a stone called meerschaum, to adhesive slate, abestos, rock cork, and other minerals; and to raw silk and wool. The following general principles are deducible from the experiments of Saussure\*.

1. It is necessary to deprive the solid of the air which it naturally contains. When of a nature not to be injured by heat, this is most effectually done by igniting the solid, and quenching it under mercury, where it is to be kept, till admitted to a given volume of the gas to be absorbed. Solids that are decomposible by heat may be deprived, though less effectually, of air, by placing them under a receiver, which must then be exhausted by the air pump.

2. The same solid absorbs different quantities of different gases. Charcoal for instance condenses 90 times its bulk of ammoniacal gas,

and not quite twice its bulk of hydrogen.

3. Solids; chemically the same, absorb different quantities of the same gas, according to their state of mechanical aggregation. Thus the dense charcoal of box-wood absorbed 7½ volumes of air, while a light charcoal prepared from cork, did not absorb a sensible quantity.

4. Different solids absorb different quantities of the same gas; the quantity of carbonic acid absorbed by charcoal being about seven

times greater than that absorbed by meerschaum.

5. When the solid exerts no chemical action on the gas, the ab-

sorption is terminated in 24 or 36 hours.

6. The effect of moistening the solid is to retard the absorption and to diminish its amount; and when a gas has actually been absorbed, it is again driven out unchanged, partly by water of the ordinary temperature, and entirely by exposure to a boiling heat.

7. During the absorption of a gas by a solid, the temperature of the latter rises several degrees, and bears a proportion to the absorbability of the gas, and the rapidity with which it is condensed.

8. Solids condense a greater number of volumes of the more absorbable gases under a rare than under a dense atmosphere; but if the

absorption be reckoned by weight, it is most considerable under the latter state.

9. When a solid saturated with any one gas is introduced into an atmosphere of any other gas, a portion of the first is expelled, and a part of the second takes its place.

IV. Gases are absorbed by liquids. On this subject the following

general principles may be laid down.

1. The same liquid absorbs different quantities of different gases. Thus water takes up its own bulk of carbonic acid, and not one fiftieth of its bulk of hydrogen gas.

2. Different liquids absorb different quantities of the same gas. Alcohol, for instance, absorbs almost twice as much carbonic acid, as

is taken up by an equal volume of water.

3. The absorption is promoted by first freeing the liquid from air, either by long continued boiling in a vessel with a narrow neck, or by the air-pump. It requires, also, brisk and long continued agitation, especially with the less absorbable gases.

4. It does not appear that the gases are absorbed by all liquids in the same order. For example, of four gases naphtha absorbs most olefiant gas; oil of lavender most nitrous oxide; olive oil most carbonic acid; and solution of muriate of potash most carbonic ox-

ide.

5. The vicidity of liquids, though it does not much influence the amount absorbed, occasions a longer time to be spent in effecting the absorption. On the other hand, the amount of any gas which is absorbed by water, is diminished by first dissolving in the water any saline substance.

6. In general the lightest liquids possess the greatest power of absorbing gases; whereas, when there is no evident chemical action, the heaviest gases are absorbed most copiously and rapidly by the

same liquid.

7. The temperature of a liquid is raised by the absorption of a gas,

in proportion to the amount and the rapidity of the absorption.

8. In all liquids the quantities of gases absorbed are directly as the pressure. For example, a liquid, which absorbs its own bulk of gas under the pressure of the atmosphere, will still absorb its own bulk of the same gas under double, triple, &c. pressure; but its own bulk of gas, twice compressed, is equal to double its bulk of gas ordina-

rily compressed, and so on.

9. When any liquid is agitated with a limited quantity of any mixture of two gases, it does not absorb one only to the exclusion of the other, but it absorbs both. In this case, the quantities, which it takes up of each, are such, that the densities of the gases are the same in and out of the liquid, after the absorption is completed. Thus when 20 measures of pure carbonic acid are agitated with 10 of common air, at least 10 measures of gas are absorbed. But from a mixture of 20 measures of carbonic acid with 10 of common air only 3ds of 10 (=6.6) are absorbed by 10 measures of water; and the gas both in and out of the water, is two thirds carbonic acid and one third air, at the close of the experiment.

The principle, on which gases are absorbed and retained by liquids, is still a subject of controversy. By Berthollet, Thomson, Saussure, and the generality of chemists, it is ascribed to the exertion of a chemical affinity between the gas and the liquid; but it is contended by Mr. Dalton and myself that the effect in most cases is chiefly, if not wholly, mechanical. The discussion would lead me into details of too great a length; and I refer, therefore, for a statement of the argument, to two papers which I have published in the 8th and 9th volumes of Nicholson's Journal; to Mr. Dalton's New System of Chemical Philosophy; and to his reply, in the 7th vol. of Dr. Thomson's Annals, to the objections, which had been advanced against the mechanical theory, by Saussure, in the 6th volume of the same work.

V. The velocities, with which different gases, when condensed artificially by the same degree of pressure, escape through a capillary tube, has been shown by Mr. Farady to vary very considerably. The following table shows the comparative times required by some of the gases to escape from a vessel in which they were all equally compressed at the outset, till their density arrived at an atmosphere and a quarter.

Carbonic acid	l r	e(	qu	ire	be		•	٠	•	•	•		•	•	•	156.5 minutes.
Olefiant gas			•			٠										135.5
Common air																128
Coal gas																
Hydrogen .																57
	-	-		•											-	- •

These differences cease to exist at low pressures; but under the circumstances which have been stated, there seems reason to believe that the velocities, with which gases escape through capillary tubes, are inversely as their specific gravities, or in some proportion approaching this.

VI. The colour of the electric spurk, when transmitted through different gases, has been observed by De Grotthust to be as fol-

lows:

In atmospheric air of double density, the spark was more brilliant, but not coloured.

In hydrogen gas													purple.
In hydrogen gas	•	•				•				•	•	٠.	red.
-ammonia		•	•	•	•					·			red.
-dry carbonic acid gas .	•	•	•	•	•	•	•	•		•	•		violet.
- oxygen gas	•	•	•	•	•	•	•	•	•	•	•	•	ditto.
- aqueous vapour	•	•			٠	•	•	•		•	•	•	orange.
- vapour of ether? - ditto of alcohol?													colodor moor
— ditto of alcohol \	•	•	•	•	٠	•	•	•	•	•	•	•	ceration green.

The general inference from his experiments is, that the intensity

<sup>\*</sup> Journal of Science, &c. iii. 354. † 82 An. de Ch. 34.

of electric light is always in a direct proportion to the density of the gas, and in the inverse proportion to the conducting power of the

gas for electricity.

VII. The comparative soniferous properties of the gases have been determined by Messrs. Kerby and Merrick; but as these belong rather to mechanical than to chemical science, I shall content myself with referring to the account of them in the 27th and 33d volumes of Nicholson's Journal, and in the 45th volume of the Philosophical Magazine.

### SECTION II.

### Oxygen Gas.

WE have no knowledge of the properties of oxygen in a state of complete separation. In the most simple form, under which we can procure it, it is combined with caloric, and probably with light and electricity, constituting oxygen gas.

1. Oxygen gas may be procured from various substances.

1. From the black oxide of manganese, heated to redness in a gunbarrel, or in an iron or earthen retort; or, from the same oxide, heated by a lamp in a retort or gas bottle, with half its weight of strong sulphuric acid.

2. From the red oxide of lead (the common red lead used by paint-

ers), heated either with or without sulphuric acid.

3. From various other oxides, as will be hereafter mentioned.

4. From nitrate of potash (common saltpetre) made red-hot in a

gun-barrel, or in an earthen retort.

5. From oxy-nuriate of potash, heated in a small glass retort, over an Argand's lamp. The oxygen gas thus produced, is much purer than that obtained in any other mode, especially the last portions, which should be kept separate.

All these substances, after having yielded oxygen gas, are found considerably diminished in weight; and calculating each cubic inch of gas to be equal to one third of a grain, the loss of weight will be

found pretty exactly equivalent to that of gas generated.

II. This gas has the following properties:

1. It is not absorbed by water\*; or, at least, is so sparingly absorbed, that, when agitated in contact with water, no perceptible diminution takes place.

2. It is rather heavier than common air. Sir H. Davy originally stated 100 cubic inches at 55° Fahrenheit, and 30 inches of the baro-

In this as in several other instances, where a gas is said not to be absorbed by water, the assertion is not to be taken strictly, but merely as implying that only a minute and difficultly appreciable portion is absorbed. The precise proportion of each gas absorbed by water is stated in chap. vi. sec. iii. in the form of a table.

meter, to weigh 35.06 grains; and at the temperature of 60°, the same quantity would weigh 34.70, or, according to the same author, in his Elements of Chemical Philosophy, 34 grains. Messrs. Allen and Pepys have determined 100 cubic inches to weigh 33.82 grains, the barometer being 30, and thermometer 60°. By Biot and Arago its specific gravity is stated to be 1.10359.

3. All combustible bodies burn in exygen gas with greatly increas-

ed splendour.

(a) A lighted wax taper, fixed to an iron wire, and plunged into a vessel of this gas, burns with great brilliancy, pl. iv. fig. 38. If the taper be blown out, and let down into a vessel of the gas while the snuff remains red hot, it instantly rekindles, with a slight explosion.

(b) A red-hot bit of charcoal, fastened to a copper wire, and im-

mersed in the gas, throws out beautiful sparks.

(c) The light of phosphorus, burnt in this gas, is the brightest that can be in any mode produced. Let the phosphorus be placed in a small hemispherical tin cup, which may be raised by means of the wire stand, pl. ii. fig. 25, two or three inches above the surface of water contained in a broad shallow dish. Fill a bell-shaped receiver, having an open neck at the top, to which a compressed bladder is firmly tied, with oxygen gas; and, as it stands inverted in water, press a circular piece of pasteboard, rather exceeding the jar in diameter, over its mouth. When an assistant has set fire to the phosphorus, cover it instantly with the jar of oxygen gas, retaining the pasteboard in its place, till the jar is immediately over the cup. When this has been skilfully managed, a very small portion only of the gas will excape; and the inflammation of the phosphorus will be extremely brilliant. The expanded gas rises into the flaccid bladder, and is thus prevented from escaping into the room, and proving disagreeable by its suffocating smell.

(d) Substitute, for the phosphorus in experiment c, a small ball formed of turnings of zinc, in which about a grain of phosphorus is to be inclosed. Set fire to the phosphorus, and cover it expeditiously with the jar of oxygen. The zinc will be inflamed, and will burn with a beautiful white light. A similar experiment may be made with metallic arsenic, which may be moistened with spirit of turpentine. The filings of various metals may also be inflamed, by placing them in a small cavity, formed in a piece of charcoal, igniting the charcoal, and blowing, on the part containing the metal, a

stream of oxygen gas.

(e) Procure some thin harpsichord wire, and twist it round a slender rod of iron or glass, so as to coil it up in a spiral form. Then withdraw the rod, and tie a little thread or flax round one end of the wire, for about one 20th of an inch; which end is to be dipped into melted sulphur. The other end of the wire is to be fixed into a cork; so that the spiral may hang vertically (fig. S9). Fill, also, with oxygen gas, a bottle capable of holding about a quart, and set it with its mouth upwards. Then light the sulphur, and introduce the wire into the bottle of gas, suspending it by the cork. The iron will burn with a most brilliant light, throwing out a number of sparks,

which fall to the bottom of the bottle, and generally break it. This accident, however, may frequently be prevented by pouring sand into the bottle, so as to lie about half an inch deep on the bottom (see pl. iv. fig. 39). According to Mr. Accum\*, a thick piece of iron or steel, such as a file, if made sharp pointed, may be burnt in oxygen gas. A small bit of wood is to be stuck upon its extremity, and set on fire, previously to immersion in the gas.

(f) A little of Homberg's pyrophorus, a substance to be hereafter described, when poured into a bottle full of this gas, immediately

flashes like inflamed gunpowder.

From this detail of its properties, it appears, therefore, that oxygen gas is eminently a supporter of combustion. It was long, indeed, supposed to be the only supporter, and the presence of oxygen was imagined to be essential to combustion. It will appear, however, in the sequel, that other simple bodies, capable of existing in an aërial form, are equally entitled to rank as supporters of combustion. Among these are chlorine, iodine, and possibly fluorine. But they do not all support the combustion of the same substances; charcoal, for example, does not burn in chlorine, and potassium is the only

body that is known to burn in the vapour of iodine.

III. During every combustion in oxygen gas, the gas suffers a considerable diminution.—To exhibit this, experimentally, in a manner perfectly free from all sources of error, would require such an apparatus as few beside adepts in chemistry are likely to possess. The apparatus required for this purpose is described in the 6th chapter of Lavoisier's Elements. The fact may, however, be shown, less accurately, in the following manner: Fill, with oxygen gas, a jar of moderate size, which has a neck and ground-glass stopper at the top. Then, with the assistance of a stand, formed of bent iron wire (pl. ii. fig. 25), place a shallow tin vessel, containing a bit of phosphorus or sulphur, three or four inches above the level of the water of a pneumatic trough. Invert the jar of oxygen gas, cautiously, and expeditiously, over this cup, so as to confine it, with its contents, in the gas, and, pressing down the jar to the bottom of the trough, open the stopper. A quantity of gas will immediately rush out, and the water will rise to the same level within the jar as without. When this has taken place, set fire to the sulphur or phosphorus by a heated iron wire, and instantly put in the stopper. The first effect of the combustion will be a depression of the water within the jar; but when the combustion has closed, and the vessel has cooled, a considerable absorption will be found to have ensued.

Those persons who are possessed of a mercurial apparatus may repeat this experiment in a less exceptionable manner. On the surface of the quicksilver let a small hemispherical cup float, made of untinned sheet-iron; and, in order to keep it from the sides of the jar, it may rest on a wire stand, shaped like the figure 43, plate iv. Let a jar, the height and diameter of which must be regulated by the size of the mercurial trough, be filled with oxygen gas over wa-

<sup>\*</sup> Nicholson's Journal. 8vo. i. 320.

ter, and be removed, by means of a piece of pasteboard, as before described, to the mercurial bath, inverting it dexterously over the tin If the phosphorus had been previously set on fire, a large quantity of the gas, expended by the heat, would have escaped, and would have prevented the accurate measurement of the absorption. After drying the surface of the mercury within the jar by blotting paper, a portion of the included gas must, therefore be removed. This is done by an inverted syphon, one leg of which is to be introduced (in the same manner as is shown at fig. 41, g) within the jar before placing it over the mercury; and the gas will be forced through the open extremity of the other, when the jar is pressed down into the quicksilver. When the proper quantity has been expelled, remove the syphon. The cup, containing the phosphorus, will thus rest on the surface of the quicksilver within the jar, and above the level of the mercury without. The phosphorus is to be inflamed by passing a crooked iron wire, made red hot, through the quicksilver. On the first impression of the heat arising from its combustion, the included gass will be considerably expanded; but when the phosphorus has ceased to burn, a considerable absorption will be found to have taken place, the amount of which may be measured by ascertaining the height of the quicksilver within the jar, before and after the experiment. The quantity of phosphorus employed should be very small, and should not bear a greater proportion than that of 10 grains to each pint of gas; otherwise the combustion will go on so far as to endanger the breaking of the jar, by the approach of the inflamed phosphorus.

In this process, a white dense vapour is produced, which condenses on the inner surface of the jar in solid flakes. This substance has strongly acid properties; and, being formed by the union of oxygen

with phosphorus, is termed the phosphoric acid.

The diminution of the volume of oxygen gas, by the combustion of other bodies, may be ascertained in a similar manner. When the substance employed is not easily set on fire, it is proper to enclose, along, and in contact with it, a small bit of phosphorus, the combustion of which excites sufficient heat to inflame iron-turnings, charcoal, &c. In the instance of charcoal, however, though that substance undergoes combustion, no absorption ensues; because, as will appear in the sequel, the product is a gas, occupying exactly the same bulk as the oxygen gas submitted to experiment.

IV. All bodies, by combustion in oxygen gas, acquire an addition to their weight; and the increase is in proportion to the quantity of gas absorbed, viz. about one third of a grain for every inch of gas.—To prove this by experiment, requires also a complicated

apparatus.

But sufficient evidence of this fact may be obtained by the following very simple experiment. Fill the bowl of a tobacco pipe with iron wire coiled spirally, and of known weight: let the end of the pipe be slipped into a brass tube, which is screwed to a bladder filled with oxygen gas: heat the bowl of the pipe, and its contents, to redness in the fire, and then force through it a stream of oxygen gas from the bladder. The iron wire will burn; will be rapidly oxy-

dized; and will be found, when weighed, to be considerably heavier than before. When completely oxydized in this mode, 100 parts of

iron wire gain an addition of about 30.

V. Every substance, capable of union with oxygen, affords, by combustion, either an oxide, an acid, or an alkali.—When a body, by being burnt in oxygen gas, affords a compound, which has none of those qualities that characterize acids or alkalies, we denominate this product an oxide. If we collect, for example, the iron wire, which was burned in the last experiment, we shall find that it has lost all its metallic qualities, and has become a brittle, dark-coloured substance totally destitute of lustre and of taste, and termed an oxide of iron. But if, instead of iron wire, we had burned a quantity of sulphur in oxygen gas, over water, the result would have been that the water, which confined the gas, would have become acid or sour. Potassium, on the contrary (one of the new metals discovered by Sir H. Davy), would have yielded an alkali under the same circumstances. Hence the extensive class of combustible bodies may be subdivided into three orders; 1st, those which afford oxides by combination with oxygen; 2dly, those which yield acids; and 3dly, those which give alkalies. In many instances, however, a body is capable of passing through the intermediate state of an oxide, before it is converted either into an acid or an alkali.

VI. Oxygen gas supports, eminently, animal life.—It will be found that a mouse, bird, or other small animal, will live four or five times longer in a vessel of oxygen gas, than in one of atmospherical

air of the same dimensions.

VII. This effect seems connected with the absorption of oxygen by the blood.—Pass up a little dark-coloured blood into a jar partly filled with oxygen gas, and standing over mercury. The gas will be in part absorbed, and the colour of the blood will be changed to a bright and florid red. This change to red may be shown, by putting a little blood into a common vial filled with oxygen gas, and shaking it in contact with the gas.

### SECTION III.

#### Chlorine Gas.

I. This gas may be found by either of the following processes:

Process 1. Into a stopper retort introduce eight ounces of liquid muriatic acid, and four ounces of finely powdered manganse, and apply the heat of a lamp. A gas will be produced, which may be received, in the usual manner, over water of the temperature of 80° or 90° Fahrenheit. From the foregoing materials about 160 cubical inches of gas may be obtained.

- Process 2. Grind together in a mortar eight ounces of muriate of soda (common salt) with three ounces of powdered manganese; put

them into a stoppered retort, and pour on them four ounces of sulphuric acid, which have been diluted previously with four ounces of water, and suffered to cool after dilution. Or the proportions recommended by Thenard may be employed, viz. 1750 muriate of soda, 450 oxide of manganese, water and sulphuric acid each 800. On applying a gentle heat gas will be produced, as in Process 1. But as the gas is absorbed by contact with cold water, though not rapidly, it should be received, when it is intended to be kept, in bottles filled with, and inverted in, water of the temperature of 80° or 90° Fahr. and provided with accurately ground stoppers. The stoppers must be introduced under water, while the bottle remains quite full of the gas, and inverted, and no water must be left in the bottle, along with the gas.

II. Chlorine gas has the following properties:

(a) It has a vellowish green colour: and this property has suggest-

ed the name chlorine\*.

(b) It has a pungent and suffocating smell. In experiments on this gas, great care should be taken that it does not escape, in any considerable quantity, into the apartment; for its action on the lungs

is extremely oppressive and injurious.

(c) It is heavier than common air (taking the statement of Gay Lussac) in the proportion of 2470 to 1000 by experiment, or 24216 by calculation; and 100 cubic inches should, therefore, weigh 75.33 grains. Sir H. Davy finds them to weigh between 76 and 77 grains, at a mean temperature and pressure, which would make its specific gravity 2.5082.

(d) By a temperature of + 40° Fahr. it is reduced into a liquid form, and is condensed on the sides of the vessel. But if the gas be previously dried by exposure to muriate of lime, it bears a cold

of 40° below 0 without condensation\*.

When a receiver, filled with this gas, not artificially dried, is surrounded by snow, or pounded ice, the gas forms on its inner surface of solid concretion, of a yellowish colour, resembling, in its ramifications, the ice which is deposited on the surface of windows during a frosty night. By a moderate increase of heat, such as to 50° Fahrenheit, this crust melts into a yellowish, oily liquid, which, on a farther elevation of temperature, passes to the state of a gas.

(e) Chlorine gas, in its ordinary state, destroys all vegetable colours. This may be shown by passing, into the gas confined by water, a piece of paper stained with litmus, the colour of which will immediately disappear. Hence the application of this gas to the purpose of bleaching, its power of effecting which may be shown by confining, in the gas, a pattern of unbleached calico, which gas, has been previously boiled in a weak solution of caustic potash, and then washed in water, but not dried. Chlorine gas, however, which has been carefully dried by solid muriate of lime, and into which per-

Vol. I.-R

<sup>\*</sup> From χλωρος green.
† Sir H. Davy, Phil. Trans. 1811. p. 30.

fectly dry litmus paper is introduced, produces no change of colour in the litmus, a sufficient proof that its bleaching power depends on the presence and decomposition of water.

(f) This gas is absorbed by water; slowly, if allowed to stand

over it quiescent, but rapidly when agitated.

1. The best method of effecting the impregnation of water with this gas, is by means of a Woulfe's apparatus, the bottles of which should be surrounded by ice-cold water. The quantity of the gas, which water is capable of absorbing, appears, from the concurrent testimony of Davy and Dalton, to be twice its bulk. The former has lately remarked that water, apparently saturated with chlorine by agitation with it in a narrow vessel, takes up more of the gas when exposed to it with a broad surface.

2. The watery solution, if perfectly free from common muriatic acid, has not the usual taste of an acid, but an astringent one. Its purity from muriatic acid may be ascertained by a solution of nitrate

of mercury, which is not precipitated by pure chlorine.

3. The watery solution has the colour and peculiar smell of the gas, and has a similar property of discharging vegetable colours.

Hence it may be employed in bleaching.

- 4. When the watery solution of chlorine is exposed to a temperature only a little above that of freezing water, the gas, which is combined with it, separates in the form of a liquid, heavier than water.
- 5. Chlorine is not altered by the temperature of boiling water; for its solution may be raised in distillation, and again condensed without change.

When the solution of chlorine in water is exposed to the direct rays of the sun, oxygen gas is obtained, and the acid passes to

the state of muriatic acid.

Chlorine is susceptible of combination with various other bodies, and the compounds possess, in many instances, remarkable properties. These will be made the subject of a distinct chapter in a subsequent part of the work.

### SECTION IV.

# Nitrogen or Azotic Gas.

AFTER separating, from any quantity of atmospherical air, all the oxygen which it contains, there remains a gas which was called by Lavoisier azotic gas, a name applied to it in consequence of its unfitness for supporting animal life; and derived from the Greek privative a and to vita. This, however, as being merely a negative property, has since been deemed an improper foundation for its nomenclature: and the term nitrogen gas has been substituted; because one of the most important properties of its base is, that by

union with oxygen it composes nitric acid. By this appellation

therefore, I shall hereafter distinguish it.

I. Nitrogen gas may be procured, though not absolutely pure, yet sufficiently so for the purpose of exhibiting its general properties, in any of the following manners: 1. Mix equal weights of iron filings and sulphur into a paste with water, and place the mixture, in a proper vessel, over water, supported on a stand: then invert over it, a jar full of common air, and allow this to stand exposed to the mixture for a day or two. The air contained in the jar will gradually diminish, as will appear from the ascent of the water within the jar, till at last only about four 5ths of its original bulk will remain. The vessel containing the iron and sulphur must next be removed, by withdrawing it through the water; and the remaining air may be made the subject of experiment.

2. A quicker process, for procuring nitrogen gas, consists in filling a bottle, about one 4th, with the solution of nitrous gas in liquid sulphate of iron, or with liquid sulphuret of lime, and agitating it with the air which fills the rest of the bottle. During the agitation, the thumb must be firmly placed over the mouth of the bottle; and, when removed, the mouth of the bottle must be immersed in a cup full of the same solution, which will supply the place of the absorbed air. The agitation, and admission of fluid, must be renewed,

alternately, as long as any absorption takes place.

S. Atmospheric air, also, in which phosphorus has burned out, affords, when time has been allowed for the condensation of the

phosphoric acid, tolerably pure nitrogen gas.

4. Azotic gas may be procured from the lean part of flesh meat (beef for example), which may be put into a gas bottle, along with very dilute nitric acid. By a heat of about 100°, the gas is disengaged, and may be collected over water. Its source has been satisfactorily traced to the animal substance, no part of it proceeding from the nitric acid.

II. Nitrogen gas has the following properties;

1. It is not absorbed by water.

\_\_\_\_\_

2. It is a little lighter than atmospheric air, 100 cubic inches being found by Sir H. Davy to weigh 30.04 grains under a pressure of 30 inches, and at the temperature of 55° Fahrenheit. At 60° Fahrenheit 100 inches weigh, therefore, 29.73 grains. According

to Biot and Arajo, its specific gravity is 0.96913.

3. It immediately extinguishes a lighted candle, and all other burning substances. Even phosphorus, in a state of active inflammation, is instantly extinguished when immersed in nitrogen gas. This is best shown by placing the burning phosphorus in a tin cup, raised by a stand over the surface of the water, and quickly inverting over it a jar filled with nitrogen gas.

4. It is fatal to animals that are confined in it.

5. When mixed with pure oxygen gas, in the proportion of four parts to one of the latter, it composes a mixture resembling atmospheric air in all its properties. Of this any one may be satisfied, by mixing four parts of azotic gas with one of oxygen gas, and im-

mersing, in the mixture, a lighted taper. The taper will burn as in atmospherical air.

### Composition of Nitrogen.

That nitrogen is not an element, but itself a compound, has been long suspected, and various attempts have been made to discover its ingredients. Some of the facts, which have been supposed to throw light on its nature, I shall reserve for the chapter of ammonia, because they will be better understood in connection with that subject.

Berzelius, from the combination of experiment with much theoretical reasoning, has deduced, that nitrogen is compounded of oxygen and an unknown base, in the following proportions\*:

Base ... 44.32 ... 79.64 ... 100.00 Oxygen .. 55.68 ... 100 ... 125.51

179.64

This base, it must be observed, however, is purely hypothetical; and, as it has never yet been exhibited in a separate state, we cannot at present know any thing of its properties. Berzelius has proposed for it the name of *nitricum*.

100

A series of experiments to prove the composition of nitrogen by synthesis, has been published in the 4th volume of Dr. Thomson's Annals, by Mr. Miers, of London. He attempted to deprive water of part of its oxygen by transmitting it, along with sulphurated hydrogen, through an ignited copper tube; by which process he obtained a mixture of oxygen and nitrogen gases, in proportions the same as those constituting atmospheric air. If no source of fallacy existed in the experiment, it would follow that nitrogen is composed of oxygen and hydrogen, with less oxygen than exist in water. But the experiments, though ingeniously devised, require the most careful repetition, before so important a conclusion can be established: and there is reason to suspect, from the nature of the products, that atmospheric air must, by some means, have found its way into the apparatus. It is remarkable, however, that the proportions of the elements of ammonia, deduced by Mr. Miers from his experiments, precisely agree with the hypothetical proportions assigned by Berzelius, viz. 55.6 oxygen and 44.4 hydrogen per cent. in weight.

The experiments of Sir H. Davyt, directed to the decomposition of nitrogen, on the presumption of its being an oxide, have not been attended with any better success. Potassium was ignited, by intense Voltaic electricity, in nitrogen gas; and the result was, that hydrogen appeared, and some nitrogen was found deficient. This, on first view, would lead to the suspicion, that nitrogen was decomposed. But, in subsequent experiments, in proportion as the potassium was more free from a coating of potash, which would introduce water, so, in proportion, was less hydrogen evolved, and less

nitrogen found deficient. The general tenor of these inquiries, therefore, lends no strength to the opinion, that nitrogen is a compound body.

#### SECTION V.

### Atmospheric Air.

THE air of our atmosphere, it appears, from the facts stated in the preceding section, is a mixture of two different gases, viz. oxygen gas and azotic gas. The former of these seems to be the only ingredient on which the effects of the air, as a chemical agent, depend. Hence combustible bodies burn in atmospheric air, only in consequence of the oxygen gas which it contains; and, when this is exhausted, air is no longer capable of supporting combustion\*. Its analysis is most satisfactorily demonstrated by the action of heated mercury, as explained by Lavoisier, in the third chapter of his Elements of Chemistry. By exposure, during 12 days, to mercury heated in a retort, a given quantity of atmospheric air was found to be diminished in bulk, and to have lost its property of supporting combustion. The mercury, also, had suffered a considerable change; a part of it was no longer a shining fluid metal; but was changed into red scaly particles; and its weight was, also, increased. These red particles were collected, and distilled in a retort; by which operation a quantity of oxygen gas was evolved, precisely equal in bulk to what the air had lost in the first part of the experiment. These results afford the most satisfactory evidence, that the air of our atmosphere is composed of two distinct fluids. The one is capable of yielding its base to mercury; and, when separate, is eminently adapted to the support of combustion and of animal life, the other is not absorbable by mercury, and is destitute of both those important qualities.

The details of this method of analyzing atmospheric air I omit on account of the extreme tediousness of the process. Sufficient evidence of its composition may be obtained, however, much more

expeditiously, by the following experiments.

I. Burn a little sulphur or phosphorus, in the manner described, sect. ii. substituting, for oxygen gas, common atmospherical air. The combustion will, in this instance, be less vivid; will cease sooner; and the absorption, when the vessels have cooled, will be much less considerable than in the former case.

The phosphorus, however, will have absorbed the whole of the oxygen gas contained in the air submitted to experiment; and

<sup>\*</sup> Certain combustible bodies even cease to burn in atmospheric air, long before its oxygenous portion is consumed, for reasons that will hereafter be given.

hence it may be employed for measuring the quantity of oxygen gas in a given bulk of atmospherical air. This may be accomplished, either by its slow or rapid combustion. Berthollet proposes\* to expose a cylinder of phosphorus, fastened to a glass rod, in a narrow glass vessel, graduated into equal parts, and standing full of air over water. (See fig. 24.) The phosphorus immediately begins to act without visible combustion on the included air; and in six or eight hours its effect is completed. The residuary azotic gas has its bulk enlarged about one 40th, by absorbing a little phosphorus; and for this allowance must be made in measuring the diminution.

In the eudiometer of Seguin, the rapid combustion of phosphorus is employed with the same view. A glass tube, open at one end only, about an inch in diameter, and eight or ten high, is filled with, and inverted in, mercury. A small bit of phosphorus, dried with blotting paper, is then introduced, and, by its inferior specific gravity, rises to the top of the tube where it is melted, by bringing a redhot poker near to the outer surface of the glass. When the phosphorus is liquefied, a measured portion of the air to be examined is admitted, by a little at once, into the tube. The phosphorus inflames at each addition, and the mercury rises. When all the air under examination has been added, the red-hot poker is again applied to secure the completion of the process, and the residuary gas is transferred into a graduated measure, where its bulk is carefully ascertained. In this instance, about one 40th the volume of the residuary gas is to be deducted from the apparent quantity of azotic gas, because, in this case also, a small portion of phosphorus is dissolved by the latter, and occasions a trifling expansion. With this deduction, atmospheric air loses pretty accurately 21 parts out of every 100; and contains, therefore, 21 per cent. of oxygen, and 79 of azote by measuret. And it is remarkable, that no appreciable difference exists between the proportions of oxygen and azote in the atmospheres of distant places; from which it appears, that the purity and salubrity of air depend on some other circumstances than the proportion of these its chief elements.

as, for supporting combustion, may be shown, also, by a comparative experiment with two candles. Provide a circular piece of lead, three inches diameter, and half an inch thick, from the centre of which proceeds a perpendicular iron wire, six or eight inches high; to the end of this wire fasten a piece of wax taper. Set the candle, supported by its stand, on the shelf of a pneumatic cistern; and place, also, the conducting pipe from the bladder (e, fig. 41), in the position shown by the figure; the cock d, however, being shut. Then, having the syphon g in the inverted position shown in the plate, sink the whole apparatus into the water. Part of the air in the jar a will escape through the syphon, and will be replaced by water.

<sup>\*</sup> Annales de Chimie, xxiv. 78.

<sup>†</sup> Various other methods of analyzing atmospherical air will be described in the course of the work. Reference to them may found in the Index, article Eudiometer.

When we have left, in the jar, the proper quantity of air, the syphon must be removed, and the jar returned to its place. The level of the water will now be considerably higher within than without the receiver; and its height must be noted. On passing a succession of electrical sparks from the conducting wire to the bent pipe, and opening the  $\cos d$  from the bladder filled with hydrogen gas, we shall have a small flame, which is to be extinguished as soon as, by its means, we have lighted the candle. The candle may be suffered to burn till it is extinguished; and the duration of its burning, and the diminution it occasions in the air, are to be noted. When the combustion is repeated in the same manner, but with the substitution of oxygen gas, it will be found to last considerably longer, and

the diminution of volume in the gas will be much greater.

The same fact may be demonstrated, but less accurately, by a Provide two jars each two inches in diameter, simple apparatus. and 12 inches long, and each having a neck at the top with a compressed bladder tied upon it. Fill one of the jars, leaving the bladder empty, with oxygen gas; and, at the same instant, with the aid of an assistant, invert both jars over the burning candles, keeping the oxygen gas in its place till the jar is inverted, by a piece of pasteboard. In the common air, the candle will soon be extinguished; but that confined in oxygen gas will burn with much greater splendour, and will continue burning long after the other is extinguished. On the first impression of the flame, a quantity of expanded gas will rise into each bladder, which is to be pressed out at the close of the experiment, in order that the absorption may be compared in both The diminution in the jar of the oxygen gas will be found greatly to exceed that of the common air.

III. Take two tubes, each a few inches long, closed at one end, and divided into 100 aliquot parts. Fill the one with atmospherical air, the other with oxygen gas, and invert them in two separate cups filled with a solution of sulphuret of potash. The sulphuret will ascend gradually within the tube of common air, till, after a few days, about four 5ths of its original volume will remain; but, in that containing oxygen, it will ascend much higher, and if the gas be pure,

will even absorb the whole.

The explanation of this fact is, that liquid sulphuret of potash has the property of absorbing oxygen but not nitrogen. It therefore acts on atmospheric air only as long as any oxygen gas remains, and may be employed as a means of ascertaining the quantity of this gas in the atmosphere at different times and at distant places. An improved instrument\*, thus graduated, has been employed by Guyton as an Eudiometer\*. But an apparatus, of much greater simplicity, and facility of application, is that of Professor Hope, of Edinburgh, announced in Nicholson's Journal, 8vo. iv. 210. It consists of a small bottle, of the capacity of 20 or 24 drachms (fig. 20. pl. ii), destined to contain the eudiometric liquid, and having a small stopper at b. Into the neck

† Other eudiometers will be described hereafter.

See Nicholson's Philosophical Journal, 4to. i. 268; or Tilloch's Philosophical Magazine, iii. 171.

of the bottle a tube is accurately fitted by grinding, which holds precisely a cubic inch, and is divided into 100 equal parts. the apparatus, the bottle is first filled with the liquid employed, which is best prepared by boiling a mixture of quicklime and sulphur with water, filtering the solution, and agitating it for some time in a bottle half filled with common air. The tube filled with the gas under examination (or with atmospherical air, when the quality of this compound is to be ascertained), is next to be put into its place; and on inverting the instrument, the gas ascends into the bottle, where it is to be brought extensively into contact with the liquid by brisk agitation. An absorption ensues; and, to supply its place the stopper b is opened under water, a quantity of which rushes into the bottle. stopper is replaced under water; the agitation renewed; and these operations are performed alternately, till no farther diminution takes The tube a is then withdrawn, the neck of the bottle being under water, and is held inverted in water for a few minutes; at the close of which the dimiuntion will be apparent. Its amount may be measured by the graduated scale engraved on the tube.

To the eudiometer of Dr. Hope there are, however, a few objec-If the tube a and the stopper b are not both very accurately ground, air is apt to make its way into the instrument, to supply the partial vacuum, occasioned by the absorption of oxygen gas. This absorption occasions a diminished pressure within the bottle; and, consequently, towards the close of each agitation, the absorption goes on very slowly. Besides, the Eudometric liquid is constantly becoming more dilute by the admission of water through b. obviate all these difficulties, I have substituted for the glass bottle, one of elastic gum, as shown by fig. 21, b. The tube a is accurately ground into a short piece of very strong tube of wider bore, as shown at c, the outer surface of which is made rough by grinding, and shaped as represented, that it may more effectually retain the neck of the elastic bottle when fixed by a string. This instrument is used, in every respect, in the same way as Dr. Hope's. The only difficulty is, in returning the whole of the residuary gas into the tube; but

the art of doing this will be acquired by practice.

An ingenious modification of the eudiometer, which enables us to measure an absorption of only  $_{75}^{6}$  part of the gas employed, is described by Mr. Pepys, in the Philosophical Transactions for 1807,

or Philosophical Magazine, xxix.

IV. Atmospheric air supports animal life, only in consequence of the oxygen gas which it contains.—Air, after having been received into the lungs, and again expired, is found to have lost a considerable part of its oxygen, viz. from 10 to 12 per cent. It proves fatal to animals, however, long before this ingredient is wholly exhausted; and hence it appears, that a considerable portion of oxygen gas is necessary to fit the air for supporting respiration. As the analysis of expired air requires an acquaintance with another gas, not hitherto described, viz. carbonic acid, its examination will be postponed to a future occasion.

V. Atmospheric air is diminished in volume by animal respiration. This may be shown by repeating a very simple experiment, originally contrived by Mayow. He confined a mouse in a small glass jar, and tied the jar over, quickly and firmly, with moistened bladder. The heat of the animal first expanded the air, and rendered the bladder convex outwards; but when the animal after death had become cold, the bladder exhibited a hollow surface, proving that the air within was diminished in its bulk.

The exact amount of the diminution may be shown, by confining a mouse, over water, in a graduated jar, furnished with a stop-cock, and containing common air. As the heat of the animal, however, would occasion the expulsion of part of the air, it is expedient, on first depressing the jar into water, to open the cock, through which a part of the air will escape: the cock is then to be shut, and the height of the water within to be accurately noted. At first, the level will be depressed, in consequence of the expansion of the air by the warmth of the animal; but, after its death, a considerable di-

minution will be observed.

VI. The weight of 100 cubic inches of atmospheric air, at 60<sub>0</sub> Fahrenheit and 30 inches barometer, is said by Mr. Kirwan to be 30.92 grains. Sir H. Davy states it, when under the same pressure, but at 55° Fahrenheit, to be 31.10 grains, from which may be deduced that with the temperature and pressure assumed by Mr. Kirwan 100 inches would weigh 30.78 grains. Under the same circumstances, Sir George Shuckburgh's experiments fix its weight at 30.5 grains; and this is probably the most correct determination.

#### SECTION VI.

# Hydrogen Gas.

The most simple form, in which hydrogen has hitherto been obtained, is in that of a gas, or in a state of union with caloric, and perhaps with electricity and light. From this combination we are not able to separate it, except by availing ourselves of the affinity of some other substance, in which case the hydrogen separates from the caloric, and forms, with the body which has been added, a new combination. Of its nature, we know but little; but as it has not yet been resolved into any more simple form, it is still arranged among elementary bodies. From the recent experiments of Sir H. Davy (which will be described under the article ammonia), it appears not improbable that hydrogen is a metallic body.

The most important compound of hydrogen, and the only one which will be noticed at present, is that which it affords by union with the base of oxygen gas. It is on its affinity for this base that all the properties depend, which are illustrated by the following experiments. Much of the force of this attraction, it will appear pro-

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bable from the sequel, depends on its being in a state of opposite electricity to oxygen; for, in common with all inflammable substan-

ces, it is naturally in a state of positive electricity.

I. To procure hydrogen gas, let sulphuric acid, previously diluted with five or six times its weight of water, be poured on iron filings, or on small iron nails; or (what is still better) pour sulphuric acid, diluted with eight parts of water, on zinc\*, granulated by pouring it melted into cold water, and contained in a gas bottle or small retort. An effervescence will ensue, and the escaping gas may be collected in the usual manner. An ingenious apparatus for obtaining it instantaneously, in a laboratory, is described by Gay Lussac, in the 5th vol. of Ann. de Chim. et Phys. p. 300. Its construction can scarcely be understood, without the plate which accompanies it.

Hydrogen gas, thus obtained, is not, however, to be considered as absolutely pure. An observation of Mr. Cuthbertson long ago rendered it probable that, when disengaged by zinc, it contains a portion of that metal; and, when generated by means of iron, it is apt to contain a little carbureted hydrogen. Mr. Donovan has also shown t, that, when procured from zinc and dilute sulphuric acid, it is contaminated with sulphureted hydrogen and carbonic acid; and he recommends that to obtain pure hydrogen, we should first agitate common hydrogen with lime-water during a few minutes, next with a little nitrous acid, afterwards with solution of green sulphate of iron, and finally with water. It appears to me, however, that as the only impurities, discovered by Mr. Donovan, in hydrogen gas, were carbonic acid and sulphureted hydrogen, they might be equally well removed by the simple process of washing the gas either with limewater or with a solution of caustic potash.

II. This gas has the following properties:

1. It remains permanent over water, or is not absorbed in a portion exceeding  $\frac{1}{50}$ th the bulk of the water.

2. As commonly procured, it has a disagreeable smell; but pure hydrogen gas was found by Mr. Donovan to be free from all odour. This may be shown by the following ex-

periments:

3. It is inflammable.

(a) Fill a small jar with the gas, and, holding it with the mouth downwards, bring the gas into contact with the flame of a candle. The air will take fire, and will burn silently with a lambent flame. .

(b) Fill with this gas a bladder which is furnished with a stopcock, and with a small pipe, of diameter less than that of a common tobacco pipe. Press the air out through the pipe, and, on presenting a lighted candle, the stream will take fire. If this apparatus cannot be procured, a very simple contrivance will answer the purpose: break off part of an eight-ounce vial, within an inch or two from the bottom, by setting fire to a string tied round it, and moistened with spirit of turpentine. The vial will then resemble a jar with an open

† Phil. Mag. xlviii. 138.

Zinc may be purchased at the brass-founders or copper-smiths, under the name of speltre.

neck at the top. Next bore a small hole through a cork that fits the neck of the vial, and insert in it part of a common tobacco pipe, which may be fixed into the neck of the bottle, by a cement of resin and bees-wax. Then fill the bottle with water, and hold it, with the thumb pressed down on the aperture of the pipe, while hydrogen gas is passed into it. When the bottle is full of gas, remove the thumb, press the bottle down into the water, and, on the approach of a candle, the stream of air from the pipe will take fire.

Persons, who are provided with the jars represented pl. ii. fig. 22, a, may screw to the cock a brass pipe with a small aperture. On pressing the jar, filled with hydrogen gas, into the water, and opening the cock, the gas will be forced out in a stream, which may be set on fire. On this principle are founded the artificial fireworks without smell or smoke. They consist of pipes, having variously

sized apertures, some of which have a rotatory motion.

(c) In a strong bottle, capable of holding about four ounces of water, mix equal parts of common air and hydrogen gas. On applying a lighted candle, the mixture will burn, not silently, as in experiment (a), but with a sudden and loud explosion. If a large bottle be used, it should be wrapped round with a handkerchief, to prevent the glass from doing any injury, in case the bottle should be burst\*.

(d) The same experiment may be repeated with oxygen gas, instead of atmospherical air; changing the proportions, and mixing only one part of oxygen gas with two of hydrogen. The report will be considerably louder. The bottle should be a very strong one, and should be wrapped round with cloth, to prevent an accident.

(e) The same experiment may be made over water, by means of the electric spark. Procure a strong tube, about three quarters of an inch diameter, and 12 inches long, closed at one end (plate ii. fig. 29, b). About a quarter or half an inch from the sealed end, let two small holes be drilled, opposite to each other, and into each of these let a brass conductor be cemented, so that the two points may be distant from each other within the tube, about one 8th of an inch. An apparatus, serving the same purpose, and much more easily constructed, may be formed by hermetically sealing a piece of brass wire, or still better, platina wire, into the end of a glass tube (fig. 29, With this conductor, an interrupted circuit may be formed, by introducing into the tube a longer wire, one end of which terminates one 10th of an inch from the upper one, while the other extends beyond the aperture of the tube. (See fig. 84). Into this tube, standing over water, pass about half a cubic inch of a mixture of hydrogen and oxygen gases; in the proportion of two measures of the former to one of the latter. Hold the tube firmly, and pass an electric spark through the mixed gases. For relieving the shock, which is sometimes considerable on firing, an ingenious contrivance of Sir H. Davy may be employed. It is described in the Philoso-

<sup>\*</sup> These experiments may also be made advantageously, by means of an apparatus sold under the name of the inflammable air-pistol.

phical Magazine, xxxi. S. An immediate explosion will take place; after which the gases, if pure, and in the proper proportion, will be

found to have disappeared entirely.

It has been asserted by Grotthuss, that a mixture of two measures of hydrogen gas with one of oxygen, cannot be inflamed by the electric spark, when expanded to 16 times its volume by diminished pressure; nor, when dilated by heat to only six times its volume. In the latter case, even a lighted taper does not kindle, the mixture; but water is formed silently by a continued succession

of electric sparks\*.

It is rarely, however, that oxygen and hydrogen gases can be used in such a state of purity as to leave absolutely no residuum. To determine, indeed, the purity either of the oxygen or hydrogen gas employed, it is sometimes necessary so to adjust their proportions, that the whole mixture may not be condensed by firing. If, for example, we wish to know the purity of a quantity of oxygen gas, we are to use about three times its bulk of hydrogen. Let us suppose that 100 measures of oxygen are detonated with 300 of hydrogen gas, and that the total 400 is reduced by firing to 130; the diminution of volume will be 270. This number, divided by three, gives 90 for the quantity of oxygen; that is, the oxygen employed must have contained 10 per cent. of nitrogen, or of some foreign gas not condensible by hydrogen.

If atmospherical air be employed, a diminution, though not equal in amount, will be produced by the union of the hydrogen with the oxygen gas contained in the air; and if a sufficient quantity of hydrogen gas be employed, the whole of the atmospheric oxygen will thus be removed. On this principle is founded the Eudometer of Volta, which may be constructed, by graduating either of the tubes already described, into equal partst. If, in one of these tubes, we mix 300 parts of common air, and 200 of pure hydrogen gas, there will remain, after the explosion excited by passing an electric spark between the two wires, about 305 measures. There will, therefore, have been a diminution of 195 measures, of which pretty exactly one 3d may be estimated to be pure oxygen. In this instance, therefore, 65 of oxygen have been lost by 300 of air, or 21 and a fraction per cent.

The general rule for ascertaining the purity of atmospheric air by hydrogen gas, may be stated as follows: Add to three measures of the air under examination, two measures of pure hydrogen gas; inflame the mixture by electricity; observe the diminution when the vessel has cooled; and, dividing its amount by three, we obtain pretty nearly the quantity of oxygen gas which has been condensed.

In the reverse process, i. e. in determining the purity of hydrogen gas, we mix it with more oxygen, gas than is required for saturation. Suppose that to 100 of hydrogen gas we add 100 of ogygen.

<sup>\* 82</sup> An. de Chemie, 37.

<sup>†</sup> A Volta's Eudiometer, invented by Gay Lussac, is described in An. de Chim. et Phys. iv. 188.

and that 80 measures remain after detonation. The diminution will have been 120 measures; and, of these, two 3ds or 80 measures are hydrogen. Hence the inflammable gas, under examination, must contain 20 per cent. of gome other gas, which is most probably nitrogen. In this way, we determine the proportions of hydrogen and ni-

trogen in any mixture composed of those two gases only.

(f) The diminution of hydrogen and oxygen gases, by the union of their bases, may be shown also by their slow combustion. Fill a tall jar with oxygen gas, and fill also, with hydrogen gas, a bladder furnished with a stop-cock, and with a long brass pipe bent like the letter S, and drawn out to a fine point (plate iv. fig. 41). On pressing the bladder, a stream of gas will issue from the pipe, which may be set on fire, and brought cautiously under the tall inverted jar of oxygen gas. By this contrivance, the stream of hydrogen gas will be burnt in a confined portion of oxygen gas; and, on continuing the combustion a sufficient length of time, the water will be seen to rise gradually within the jar. On the first impression of the heat, indeed, a quantity of gas will escape from the jar, which will render it difficult to ascertain what degree of absorption has actually taken place. But this loss may be prevented, by using a jar with a neck at the top, to which a compressed bladder is firmly tied. The expanded air, instead of escaping through the water, will now fill the bladder at the top; and, when the experiment has closed, and the vessels have cooled, it may be ascertained, by pressing out the gas from the bladder, what quantity of oxygen gas has been consumed.

The same experiment may be more accurately and elegantly made, with the assistance of an apparatus, which I have described in the Philosophical Transactions for 1808. The description cannot be understood without the plate, which is there given, and which has been copied into the Philosophical Magazine, xxxii. and Nicholson's Journal xxi. The fact may, also, be shown by substituting, for the bladder (e, fig. 41), a small gazometer, containing a measured quantity of hydrogen gas. Let the bent pipe be screwed on the cock of the gazometer; and over its open end, placed perpendicularly, invert a jar of oxygen gas. This jar must be provided at the top with a metallic conductor, screwed into a brass cap, as represented in fig. 41: which shows also the level of the water within the jar, attained by means of a syphon. After noting the height of the water within, let a rapid succession of electric sparks be passed between the two conductors; and, on opening the cock at this instant, the stream of oxygen gas will be inflamed. The end of the pipe must then be so far depressed, that the cement of the brass cap may not be melted by the flame; and the outer surface of the top of the vessel should be kept cool. When the gas is first lighted, the oxygen gas will be suddenly expanded; but, presently, a rapid diminution will go on, till the water rises above the end of the pipe, and extinguishes the flame. If pure oxygen gas be employed, it will be found, after the experiment, uninjured in its quality, and will support the combustion of burning bodies as well as before.

When the above experiment is made, with the substitution of

common air for oxygen gas, a diminution takes place, but much less considerable, viz. not amounting to one 6th of the original bulk of the gas.

(g) When a stream of hydrogen gas is burned under a tube, 18 or 24 inches long, a musical sound is produced. The experiment may

be made in the following manner:

Into a glass bottle are put iron filings and sulphuric acid, diluted with five or six parts of water; and a cork is fitted into the neck, through which a glass tube is passed, having its upper extremity drawn out to a capillary bore. By setting fire to the hydrogen gas\*, which escapes from this extremity, a continued current or jet of flame is produced, which is allowed to pass into a tube either of glass, earthenware, or metal. If the tube be not too large, the flame becomes smaller as it is depressed; and when the tube covers the flame to a considerable depth, very clear sounds are produced. But, on the contrary, if the tube be too narrow, the flame will be extinguished; and, in proportion as the tube is enlarged, the sound diminishes; so that there is a certain limit at which it totally ceases. The same happens when the tube is too long. The sounds may be raised at pleasure, by either using tubes of various figures or dimensions, or made of different substances.

(h) It has been discovered by M. Biot that a mixture of hydrogen and oxygen gases may be made to explode by mechanical compression. A mixture of these two gases was introduced into a strong metallic syringe, furnished with a glass bottom, and a sudden stroke given to the piston. An extremely brilliant light appeared, accompanied with a loud detonation; and the glass bottom was forcibly driven out. The repetition of this experiment, it is obvious, must be attended with some difficulty and danger. The heat given out by the sudden compression of the gases is probably the

cause of the combustion which is excited.

The combustion of hydrogen and oxygen gases was many years ago successfully applied by Mr. Hare of Philadelphia to the purpose of exciting an intense heat by the blow-pipe. The peculiar construction of the apparatus cannot be understood without a plate, which may be seen in the Annales de Chemie, tom. xlv. or in the 14th volume of the Philosophical Magazine. It may be sufficient here to state, that the gases are contained each in a separate gasholder; that they are expelled by the pressure of a column of water obtained by lengthening the pipe b, fig. 36; and that their mixture does not take place, till they nearly reach the aperture of the pipe, at the extremity of which they are inflamed. This last precaution is of considerable importance, because a violent and dangerous explosion would otherwise happen. To guard the more effectually against this accident, it is adviseable to affix a valve, opening out-

‡ See Nicholson's Journal, xii. 112.

<sup>\*</sup> The gas must not be inflamed, till it has been produced for some time, and has expelled all the common air of the bottle; otherwise an explosion will happen, and the bottle will be burst, with some danger to the operator.

<sup>†</sup> See Nicholson's Journal, 8vo. i. 129, and iv. 23.

wards, in the pipe proceeding from each gas-holder, just before the junction of the two.

The power of hydrogen and oxygen gases to produce an intense degree of heat, has lately been much increased, in consequence of a suggestion of Mr. Newman to Professor Clarke of Cambridge, that the gases should be previously mixed, then condensed into a metallic reservoir, and made to pass through a capillary tube before being set on fire\*. The temperature thus produced was found adequate to the instantaneous fusion of the most refractory substances. Platinum, for instance, was not only immediately melted, but set on fire and consumed like iron wire in oxygen gas, with vivid scintillationt. Considerable danger, however, arises to the operator, from the liability of the condensed gases to explode and burst the apparatus. Several experiments have been tried for the purpose of obviating this risk, the most effectual of which, suggested by Professor Cumming, consists in interposing, between the flame and the main reservoir of gases, a cylinder containing a little water or oil, through which, by means of a valve at the bottom, the gas is allowed to passt. All, therefore, that can happen, is the explosion of the mixed gases between the inflamed jet and the surface of the oil or water, where the quantity is sufficient to occasion any serious mischief. The more effectually to guard against danger, Dr. Clark has since, on the suggestion of Dr. Wollaston interposed a fagot of capillary tubes of the smallest possible diameter, between the stop-cock, and the orifice of the pipe at which the gases are inflameds. Additional safety may, also, be given to the apparatus by interposing, between the operator and the reservoir, a strong screen, through which the piston rod of the syringe may be worked horizontally, and the flame may thus be kept up for a length of time proportionate to the size of the reservoir, from which the mixed gases are drawn . This modification of the instrument renders it applicable to some of the arts, in which not only an intense but a long continued heat is required.

4. Hydrogen gas, though inflammable itself, extinguishes burning bodies.—Bring an inverted jar, filled with this gas, over the flame of a candle; and suddenly depress the jar, so that the lighted wick may be wholly surrounded by the gas. The candle will immediately be extinguished.

5. It is fatal to animals.—This may be shown by confining, in

the gas, a mouse, or other small animal.

<sup>\*</sup> Journal of Science, &c. ii. 104.

<sup>†</sup> About twelve years before this suggestion of Mr. Newman, Platinum had been completely volatilized by the flame of the compound blow-pipe. Professor Silliman had, subsequently, often produced the same result. See the 1st part Amer. Phil. Trans.; also, Silliman's Essay in Memoirs of the Connecticut Academy, republished in Tilloch's Philosophical Magazine, London, vol. 48.

<sup>†</sup> Journal of Science, &c. ii. 379, where a plate of the improved apparatus is given.

<sup>§</sup> Thomson's Annals, ix. 327.

<sup>|</sup> Thomson's Annals, x. 373. Other improvements of the apparatus are described in the same work, x. 366.

6. It is considerably lighter than atmospherical air.—One hundred cubic inches, the barometer being 30 inches, and the thermometer 60°, weigh, according to Kirwan, 2.613 grains; according to Lavoisier, 2.372 grains; and according to Fourcroy, Vauquelin, and Seguin, 2.75 grains. The recent determination of Sir H. Davy\* is, that 100 cubic inches at 30.5 barometer, and 51° Fahrenheit, weigh 2.27 grains. Messrs. Biot and Arago ascribe to it the specific gravity of 0.07321.

(a) Let a jar filled with this gas stand, for a few seconds, with its open mouth upwards. On letting down a candle, the gas will be

found to have escaped.

(b) Place another jar of the gas inverted, or with its mouth downwards. The gas will now be found to remain a short time in the jar, being prevented from escaping upwards by the bottom and sides of the vessel.

(c) Fill, with hydrogen gas a bladder furnished with a stop-cock; and adapt to this a common tobacco pipe. Dip the bowl of the pipe into a lather of soap, and turning the cock, blow up the lather into bubbles. These bubbles, instead of falling to the ground, like those commonly blown by children, will rise rapidly into the air. On this property of hydrogen gas, is founded its application to the raising of balloons.

(d) The experiment may be varied by filling the bladder with a mixture of two parts of hydrogen gas and one of oxygen gas. Bubbles, blown with this mixture, take fire on the approach of a lighted candle, and detonate with a loud report. It is proper, however, not to set them on fire, till they are completely detached from the bowl of the pipe; otherwise the contents of the bladder will be exploded,

with considerable danger to the operator.

In this place a property of hydrogen gas may be described, which it possesses in common with all other aëriform bodies, viz. a tendency to diffusion through any other elastic fluid, with which it may be brought into contact. Common or inelastic fluids are capable of remaining in contact with each other for a long time without admixture. Thus if we half fill a wine glass with spirit of wine tinged with any colouring ingredient, and then, by means of the dropping tube, fig. 15, introduce under it a quantity of water, the spirit floats on the water, and the two surfaces remain perfectly distinct, provided we carefully avoid agitation or unequal changes of temperature. But this is not the case with elastic fluids or gases, which, it has been discovered by Mr. Daltont, penetrate each other, and become thoroughly mixed under all circumstances. The fact, with respect to hydrogen and oxygen gases, may be proved by a very simple apparatus.

Provide two glass vials, each of the capacity of about an ounce measure, and also a tube open at both ends, 10 inches long and one 20th inch bore. At each end, the tube is to be passed through a perforated

<sup>\*</sup> Phil. Trans. 1801.

<sup>†</sup> Manchester Memoirs, vol. i. new series.

cork, adapted to the necks of the vials. Fill one of the bottles with hydrogen gas, and the other with oxygen gas; place the latter on a table with its mouth upwards, and into this insert the tube secured by its cork. Then, holding the hydrogen bottle with its mouth downwards, fit it upon the cork at the top of the tube. The two bottles, thus connected, are to be suffered to remain in this perpendicular position. After standing two or three hours, separate the vials, and apply a lighted taper to their mouths, when it will almost certainly occasion an explosion in each. The hydrogen gas, though nearly 15 times lighter than the oxygen, must, therefore, have descended through the tube from the upper into the lower vial; and the oxygen gas, contrary to what might have been expected from its greater weight, must have ascended through the tube, and displaced the lighter hydrogen.

Experiments of this kind, it has been shown by Mr. Dalton, may be extended to all the other gases; but to prove the effect, tests of a different kind are necessary, which require a previous knowledge of the properties of these gases. They tend to establish the conclusion, that a lighter elastic fluid cannot remain upon a heavier with-

out an admixture of the two.

### CHAPTER VI.

OF THE COMPOSITION, DECOMPOSITION, AND PROPERTIES OF WATER.

### SECTION I.

Synthesis, or Composition, of Water.

In chap. v. sect. v. it was stated, that oxygen and hydrogen gases, when fired over water, in the proper proportion, wholly disappear. To ascertain the nature of the product thus formed, the experiment must be repeated over mercury, in a similar manner, by means of the detonating tube (pl. ii. fig. 28). When this is done repeatedly, it is found that the product of the combustion is that well known fluid, water, which is thus proved to be composed of two elementary ingredients. The water, produced in this mode, is not, however, to be considered as a compound of the two gases, but only of their bases; for the light and caloric, which constituted the gases, escape, in considerable part, during the combustion. Every gas, it must be remembered, has at least two ingredients; the one, gravitating matter, which, if separate, would probably exist in a solid or liquid form; the other, an extremely subtile fluid, termed caloric. In the example before us, caloric (and perhaps electricity and light) is a common ingre-Vol. I.—T.

dient both of hydrogen and oxygen gases; but the two gases differ, in having different bases. The basis of the one is called hydrogen of the other oxygen; and water may, therefore, be affirmed to be a compound, not of hydrogen and oxygen gases, but of hydrogen and oxygen. Its composition may be proved in two modes, by synthesis, i. e. by joining together its two elementary ingredients; and by analysis; in other words, by separating the constitutent parts of water, and again exhibiting them in a distinct form.

I. Fill, with hydrogen gas, a bladder, furnished with a stop-cock and bent pipe (fig. 41, e), as in the last chapter. Then pour into a shallow earthen dish as much quicksilver as will about half fill it, and invert over this a glass bell, full of common air and perfectly

Expel the hydrogen gas through the pipe; light the stream, and bring it under the glass bell, by raising this, and depressing it into the mercury, as soon as the inflamed gas is introduced. A portion of air will escape, at first, in consequence of the rarefaction. As the combustion continues, water will form, and will condense on the sides of the glass. This water is produced by the union of hydrogen with the oxygen contained in atmospheric air.

II. Those persons who are not possessed of a sufficient quantity of quicksilver to repeat the above experiment, may substitute the following: procure a large glass globe, capable of holding three or four quarts, and having two openings, opposite to each other, which may be drawn out for a short distance, like the neck of a retort. Inflame the stream of hydrogen gas, and introduce it into the centre of the globe. The rarefied and vitiated air will ascend through the aperture of the globe, and a constant supply of fresh air will be furnished from beneath. By this combustion, a quantity of water will be generated, which will be condensed on the inner surface of the vessel.

III. A simple and ingenious apparatus, less costly than any other, intended for the purpose of exhibiting the composition of water, is made by Mr. Cuthbertson of London. It is described and figured in Nicholson's Journal, 4to. ii. 235; or in the Philosophical Magazine, ii. 317\*; and also in plate iv. of this work, figs. 33 and 34.

In using this apparatus, however, instead of two glass receivers for the oxygen and hydrogen gases, standing inverted in a trough of water, I employ a couple of gazometers; and with this alteration, the experiment is more easily managed, as well as more striking. The apparatus, thus modified, consists of a large glass receiver or bottle a (pl. iv. fig. 34), with an opening at the bottom, into which is cemented a piece of brass, perforated with two holes. This brass piece is represented of a larger size in fig. 33; the aperture a conveying the oxygen gas, and b the hydrogen. Before commencing the experiment, the cock e, fig. 34, is screwed, by means of a collar-

<sup>\*</sup> In the same volume of the Philosophical Magazine, an interesting account may be consulted of the principal experiments on the composition of water, accompanied by neat and perspicuous engravings of the apparatus employed in them.

joint\*, to the cock b of the gazometer, fig. 35, containing oxygen gas; and to the cock d, by the same means, is affixed another gazometer,

tilled with hydrogen gas.

When it is intended to ascertain, accurately, the proportion of gases consumed and of water generated, the receiver a, previously weighed, is first exhausted by an air-pump, with which it may be connected by the female screw at c. The quantity of common air left in the receiver may be determined, by enclosing a gauge within it. If the additional expense be not deemed an objection, it is adviseable, that after exhausting the receiver, oxygen gas should be admitted; its contents be exhausted a second time; and again renewed by fresh oxygen from the gazometer, the quantity of which may be observed by the graduated scale. The receiver being thus filled with oxygen gas, and accurately closed by a cock at c, a succession of sparks is to be passed, from the prime conductor of an electrical machine, between the platina knob of the bent wire within the receiver, and the point of the brass cone. While the sparks are transmitted, the cock d is to be opened. A stream of hydrogen gas will immediately issue from the aperture at the point of the cone, and will be inflamed by the electric spark, as represented fig. 33. The cock e is now to be opened, and the size of the flame of hydrogen gas moderated by partly shutting the cock d. As the volume of hydrogen gas consumed is double that of the oxygen; and the pipe, which transmits it, is of less diameter than that conveying the latter, about twice the pressure is required to expel the hydrogen. This is given, by lessening, in that proportion, the weight of the counterpoise (ee. fig. 35) of the gazometer containing hydrogen.

During the combustion, the moveable vessel c, fig. 35, of each gazometer descends; and, by observing the graduated scales, it will be seen that the hydrogen vessel fills twice as quick as that which holds the oxygen gas. It is necessary to keep the receiver a cool by means of wet cloths; and, when this is done, the water, which is produced, will form into drops on the inside of the receiver, and collect at the bottom. At the conclusion of the experiment, the receiver is to be again weighed, and the increase noted. The quantity of gases consumed is to be observed, and their actual weight computed, by means of the table given in the Appendix. It will be found, that the weight of water produced is very nearly equal to that of the two gases expended; that is to say, for every hundred grains of water generated in the receiver, 88.3 grains of oxygen gas, and 11.7 grains of hydrogen gas (equal by measure to about 250 cubic inches of the former, and 500 of the latter), will have disappeared from the gazo-

# Of the Proportion of the Elements of Water.

meters.

The precise determination of the proportions of oxygen and hydrogen in water, is a problem of great importance, not only on account of the fact itself, but of its influence on the general theory of che-

<sup>†</sup> See pl. v. fig. 47; and the corresponding description of the structure of this joint, in the explanation of the plates at the end of the work.

mistry. The results of almost all the earliest experiments tended to prove, that water is a compound of 85 parts by weight of oxygen, and 15 of hydrogen. These numbers were afterwards corrected by Fourcroy, &c. to 85.7 of oxygen, and 14.3 of hydrogen; and in 1805 it was shown, by Humboldt and Gay Lussac, that the quantity of aqueous vapour, which gases always contain, being subtracted, it is a nearer approximation to truth to state the proportions at 87.4 and 12.6. It is admitted, on all hands, that water is formed by the union of two volumes of hydrogen gas, and one volume of oxygen gas. The greatest deviation from those numbers that has ever been contended for, is that 100 measures of oxygen gas combined with 197 of hydrogen. A difference, however, so difficult to ascertain, on account of its minuteness, may be neglected; and it may be safely assumed, that the general statement of one volume of oxygen to two of hydrogen is correct.

In determining the proportion of the elements of water, every thing will depend, therefore, on the precision with which the specific gravities of oxygen and hydrogen gases are ascertained. Taking the results of Biot and Arago as accurate (viz. 1.10359 for oxygen gas, and 0.07321 for hydrogen gas), the proportion of the elements of water must be as those numbers; and 100 grains must be composed of

Oxygen Hydrogen	•	•	•	•	:	•	•	•	•	88.286 11.714	
										-	
										100.	

These proportions scarcely differ from those determined by Berzelius (81 An. Ch. 25), viz.

Oxygen	88.246 .		100
Hydrogen	11.754 .	100	13.33
		<del></del>	
	100.	850 <b>.</b> 77	113.33

If then we admit, with Mr. Dalton, that water is compounded of an atom of oxygen united with an atom of hydrogen, the relative weights of these atoms will be the same as the relative weights of oxygen and hydrogen, ascertained to form water, viz, for oxygen very nearly 7.5, and for hydrogen 1. Or if, with Dr. Wollaston and others, we denote the atom of oxygen by 10, the atom of hydrogen will bear to 10 the same ratio that 1 bears to 7.5, viz. it will be denoted by 1.327. It should be observed, that Mr. Dalton has deduced the relative weight of the atom of oxygen to be to that of hydrogen as 7 to 1\*. But this determination is founded on the results of Humboldt and Gay Lussac, and not on the more recent, and probably more correct ones of Biot and Arago.

It must be allowed, however, to be possible, though it is a much less probable view of the subject, that water may be a compound of

<sup>\*</sup> New System, p. 275.

two atoms of hydrogen with one of oxygen, which would double the weight of the atom of oxygen, and make it 15, the number assumed by Sir H. Davy. But hitherto we have no evidence that oxygen and hydrogen unite in any other proportion, than that constituting water; for whatever excess we employ of the one gas, or of the other, the surplus invariably remains without alteration. Now it admits of being proved to be consistent with mechanical principles, that the most energetic combination of any two elements is that, in which they are united particle to particle. Until, therefore, the contrary can be established, we may assume, with Mr. Dalton, that water is a binary compound of 1 atom of oxygen, and 1 atom of hydrogen: and, adding the weights of these atoms together (7.5 + 1), an atom of water will weigh 8.5. The same proportions, expressed by dif-ferent numbers, as proposed by Dr. Wollaston, will make the relative weight of an atom of water 10.000 + 1.327 = 11.327; the only difference in this way of stating the fact, being, that oxygen, instead of hydrogen, is expressed by the decimal unit.

### SECTION II.

### Analysis, or Decomposition, of Water.

THE analytic experiments on water are of two kinds: 1st, Such as present us with one of its ingredients only, in a separate and distinct form; 2dly, Such as present us with its two component principles, the hydrogen and oxygen, mixed together in the state of gas.

I. Of the first kind are the following:

1. Procure a gun-barrel, the breech of which has been removed, so as to form a tube open at each end. Fill this with iron wire, coiled up in a spiral form. To one end of the barrel adapt a small glass retort, partly filled with water, and to the other a bent glass tube, the open end of which terminates under the shelf of the pneumatic cistern. Let the barrel be placed horizontally (or rather with that end, to which the retort is fixed, a little elevated) in a furnace, which has two openings in its body opposite to each other. (Pl. iv. fig. 40.) Light a fire in the furnace; and, when the gun-barrel has become red-hot, apply a lamp under the retort. The steam of the water will pass over the red-hot iron, and will be decomposed. Its oxygen will unite with the iron; and its hydrogen will be obtained in the form of a gas. This is the readiest and cheapest mode of procuring hydrogen gas, when wanted in considerable quantity.

2. The same experiment may be repeated; substituting an earthen tube for a gun-barrel, and weighing the iron wire accurately, both before and after the experiment. The iron will be found to have gained weight very considerably; and, if attention be paid to the weight of the water that escapes decomposition, by an addition to the apparatus (fig. 40, e), and to the weight of the hydrogen gas ob-

tained, it will be found, that the weight gained by the iron, added to that of the hydrogen gas, will make up exactly the weight of the water that has disappeared. From experiments of this kind, conducted with the utmost attention to accuracy, as well as from synthetic experiments, Lavoisier inferred, that water is compounded of 85 percent. oxygen, and 15 hydrogen, by weight, very nearly. But as hydrogen gas is eleven times lighter than common air, the proportion of gases, by volume, required to form water, is about two of hydrogen to one of oxygen gas. By the decomposition of every hundred grains of water, therefore, the iron employed gains 85 grains, and becomes oxidized; and 15 grains (equal to about 500 cubical inches) of hydrogen gas are obtained.

3. Water may be decomposed, in a similar apparatus, over charcoal instead of iron. The results, however, are different in this case,

as will appear from a subsequent section.

4. Another mode of effecting the decomposition of water yet remains to be mentioned, in which not the hydrogen, but the oxygen, is obtained in a gaseous state. This is by the action of living vegetables; either entire, or by means of their leaves only. Fill a clear glass globe with water, and put into it a number of green leaves, from almost any tree or plant. A sprig or two of mint will answer the purpose perfectly as well. Invert the glass, or place it, with its mouth downwards, in a vessel of water. Expose the whole apparatus to the direct light of the sun, which will then fall on the leaves surrounded by water. Bubbles of air will soon begin to form on the leaves, and will increase in size, till at last they rise to the top of the vessel. This process may be carried on as long as the vegetable continues healthy; and the gas, when examined, will prove to be oxygen gas, nearly pure. In this experiment, the hydrogen combines with the plant, to the nourishment and support of which it contributes, while the oxygen is set at liberty.

II. The processes, by which the elementary parts of water are separated from each other, and are both obtained in an aëriform state, as a mixture of hydrogen and oxygen gases, are dependent

on the agency of electricity.

1. The first of these experiments requires for its performance the aid of a powerful electrical machine. This fact was the discovery of a society of Dutch chemists; and the principal circumstance, in the experiment, is the transmission of electrical shocks, through a confined portion of water. The apparatus employed, in this experiment of Messrs. Dieman and Van Troostwyk, is a glass tube, about one 8th of an inch diameter, and 12 inches long, one of the ends of which is sealed hermetically, a gold wire being inserted at this end, and projecting about an inch and a half within the tube. About the distance of five 8ths of an inch from the extremity of this, another wire is to be fixed, which may extend to the open end of the The tube is next to be filled with distilled water, and to be placed inverted in a vessel of the same. When thus disposed, electrical shocks are to be passed between the two ends of the wire, through the water; and, if these shocks be sufficiently strong, bubbles of air will be formed at each explosion, and will ascend till the upper part of the wire is uncovered by the water. As soon as this is effected, the next shock that is passed will set fire to the mixed gases, and the water will rise again in the tube, a very small quantity of gas remaining. Now, as hydrogen and oyxgen gases, in a state of admixture, are the only ones that are capable of being inflamed by the electric shock; and as there is nothing in the tube, beside water, that can afford them in this experiment, we may safely infer, that the evolved hydrogen and oxygen gases arise from decomposed water.

2. An improved apparatus, exhibiting the same experiment, with less trouble to the operator, has been invented by Mr. Cuthbertson, and may be seen described and figured in Dr. Pearson's paper in the Philosophical Transactions for 1797, or in Nicholson's Journal, vols.

i. and ii. 4to.

3. The decomposition of water by galvanic electricity is a process singular adapted to demonstrate the fact in a single and elegant manner. The manner of conducting it, as well as the results, will be fully explained, when we come to treat of the general principles of electro-chemical science.

#### SECTION III.

# Properties and Effects of Water\*.

I. Water contains air.—This may be shown by placing a glass vessel of water under the receiver of an air-pump. During the exhaustion of the reciever, bubbles of air will be seen to ascend very plentifully. Much air escapes also from water, during boiling, and may be collected by a proper apparatus. The same fact may also be exhibited, by filling a barometer tube, about 32 inches long, sealed at one end, with quicksilver, except about four inches, and the remainder with water. On inverting the open end of the tube in quicksilver, bubbles of air will be seen, in a short time, to rise from the water.

The kind of gas, extricated from the water of a spring at a considerable distance from the surface, I have made the object of experiment. From 100 cubic inches of the water, or about 3½ wine pints, 4.76 cubic inches of gas were separated; of which 3.38 were carbonic acid gas, and 1.38 air of the same standard as that of the atmosphere.

† Philosophical Transactions, 1803.

<sup>\*</sup> Whenever in the course of this work, water is mentioned as an agent in any chemical operation, pure distilled water is to be understood.

It is probable that the proportion of gaseous contents differs in the water of different springs, for Mr. Dalton states the average of his experiments to be about 2 inches from 100 of water, and that the air expelled, after losing 5 or 10 per cent. of carbonic acid by the action of lime-water, consisted of 38 per cent. oxygen and 62 nitrogen\*.

Every gas is absorbed by water, deprived of all or the greater part of its air by long boiling. The quantity, however, which water is capable of absorbing, varies considerably with respect to the different gases. Those, of which only a small proportion is absorbed, require violent and long continued agitation in contact with water. The following table has been drawn up by Mr. Dalton from the combined results of his own experiments and mine.

Water absorbs, at the mean pressure and temperature of the

atmosphere,

Of carbonic acid gas	its own bull
nitrous oxide	uo.
olefiant gas	1
oxygen gas	1
nitrous gas	do.
nitrous gas Carbureted hydrogen carbonic oxide	do.
carbonic oxide	
azotic cas	do
azone gas	
azotic gashydrogen gas	do.

The accuracy of these results has been called in question by Saussuret, who, from a series of experiments of his own, has deduced the numbers expressed in the second column of the following Table.

Gases.	100 volumes of water bsorb (Dalton and Henry)	100 volumes of water
Sulphurated hydr	rogen 100	253
Carbonic acid	100	106
	100	
	12.5	
	3.7	
Carbonic oxide	1.56	6.2
Azotic	1.56	4.1
	1.56	4.8

Absolutely pure water (not merely freed from air by boiling) according to recent experiments of Mr. Dalton, takes up 2½ per cent. of its bulk of azotic gas, and two per cent. of hydrogen. In the other gases, he is disposed to abide by his original numbers, and to consider those of Saussure) as much greater than the truth.

<sup>\*</sup> New System, p. 271.

<sup>†</sup> Thomson's Annals, vii. 215.

<sup>†</sup> Thomson's Annals, vi. 340.

II. Water is contained in the air of the athosphere, even during the driest weather.—Expose to the air, in a shallow vessel, a little subcarbonate of potashor common salt of tartar. In a few days it will have become moist, or deliquiated. On the same principle, water exposed to the air, in a shallow vessel, disappears, being dissolved by the atmosphere. Saussure states the quantity of water in a cubic foot of air, charged with moisture at 65° of Fahrenheit, to be 11 grains. The quantity of water, that may be extracted from 100 cubical inches of air, at 57° Fahrenheit, is 0.35 of a grain; but, according to Clemont and Desormes, at 54° Fahrenheit, only 0.236 of a grain can be detached by exposure to muriat of lime. The experiments, both of these chemists and of Mr. Dalton, concur in proving that at the same temperature, equal bulks of different gases give up the same quantity of water to deliquescent salts. The portion of humidity, which they Whether they thus abandon, has been called hygrometric water. contain a still farther quantity in a state of more intimate union and not separable by deliquescent substances, is still undetermined.

III. Several bodies absorb water from the atmosphere, which can scarcely be supposed to have an affinity for it, and again give it up, on the application of a gentle heat. Such are almost all substances in the state of powder: porous paper; soils which have been artificially dried; parched out-meal; and even the filings of metals. Some powders retain the moisture they have absorbed, till a considerable heat is applied. The nature of this combination is not ex-

actly understood.

There are two different theories of the state in which water exists in the atmosphere and in other gases. By most writers, it has been considered as united to air by chemical affinity; and, when abstracted by other bodies, (as sulphuric acid, lime, and the whole class of deliquescent salts) the effect has been ascribed to the superior affinity of those bodies for water. Mr. Dalton first took a different view of the subject, viz. that the vapour of water, mixed with air and other gases, differs in no respect from pure steam, and is subject to the same laws. It constitutes, indeed, in his opinion, a distinct and independent atmosphere, the elastic force of which forms, at different temperatures, different proportions of the elastic force of the whole; for example, at the temperature of 65° Fahrenheit, it it gives to air 30 of its elasticity. This theory appears to have much more probability, than that which explains the phenomena by chemical affinity; and it is supported, especially, by the absorption of caloric, which is ascertained to be of the same amount in spontaneous as in forced evaporation.

Instruments for measuring the degree of moisture of the air are called hygrometers. They consist, for the most part, of some substance, such as a human hair or a fine slip of whale-bone, which is elongated by moist atmosphere, and shortened by a dry one. The extreme points are attained by placing it, first in air artificially dried, and then in air rendered as humid as possible. The degree of expansion or con-

traction is rendered more sensible by connecting it with an axis. which moves a circular index, like the finger of a clock. Mr. Les-lie, by a slight modification of his differential thermometer, makes it serve the purpose of an hygrometer; for if one of the balls be covered with silk, and then moistened with water, the rate of evaporation will be shown by the degree of cold produced, as indicated by the descent of the liquid in the opposite leg of the instrument. The drier the air, the quicker will be the evaporation, and the greater the

effect in moving the liquid within the instrument.

A new kind of hygrometer has lately been constructed by Mr. Wilson, of Dublin. It consists of the urinary bladder of a rat or other small animal, into which a thermometer tube is inserted, the bladder being afterwards filled with mercury, and tied firmly over the tube with a silk thread. The point of extreme moisture is taken by immersing the bladder in water of the temperature of 60° Fahrenheit, and that of extreme dryness, by enclosing the bulb in air, dried by contact with concentrated sulphuric acid. The interval is divided into 100 equal parts, 0 being placed at the point of extreme dryness, and 100 at that of extreme moisture. Some correction of the results obtained with this instrument is necessary, on account of the effects of changes of temperature on the bulk of the mercury\*.

IV. Water enters into combination with various solid bodies, and entirely loses its fluid form. In many instances, it unites only in a definite proportion; and it is retained by so powerful an affinity, as not to be separated by a very high temperature. Such compounds are termed hydrates, or, as Gay Lussac has proposed, hydroxurest. The pure alkalies, potash, and soda, retain, for example, even after fusion, about I their weight of water, which can only be separated, by some body having a stronger affinity for the alkali. In all hydrates. at least one atom of water must be present, or it must be contained in them in such quantity, as to bear the proportion of at leat 8.5 to the weight of the atom with which it is united. If, for example, the weight of the atom of potash be 48, as Sir H. Davy supposes, we cannot have a true chemical compound of water and potash, in which the former bears to the latter a less proportion than that of 8.5 to 48. And if, in any instance, water is obtained from a compound in a proportion less than that of the weight of the atom of water, to the weight of the atom of the body with which it is associated, we may take for granted that it is held mechanically and accidentally, and not as a true chemical constituent. Such appears to be the nature of the union of water with certain neutral salts (common salts for example) which contain only 1 or 2 per cent of their weight of water.

. V. Water dissolves a great variety of solid bodies.—The substances, on which it exerts this effect, are said to be soluble in water; and there are various degrees of solubility. See chap. i. and

the table in the Appendix.

VI. During the solution of bodies in water, a change of temperature ensues.—In most instances, an absorption of caloric (in other

Thomson's Annals, ix. 313.

words, a production of cold) is attendant on solution, as in the examples given in chap. iii. sect. 2. But, in other cases, caloric is evolved, or heat is produced. Thus, common salt of tartar, during solution in water, raises the temperature of its solvent; and caustic potash, in a state of dryness, does the same still more remarkably. Both carbonated and pure potash, however, when crystallized observe the usual law, and absorb caloric during solution. Now as their difference, in the crystalized and uncrystallized state, depends chiefly on their containing in the former, but not in the latter, water chemically combined, we may infer, that the cold, produced during the solution of salts, is occasioned by the conversion of the water, which exists in these bodies, from a solid to a liquid form. Some doubt, it must be acknowledged, is thrown on this conclusion by the obvervation of Gay Lussac, that a saturated solution of nitrate of ammonia mixed with water of the same temperature is cooled 8 or 9 degrees\*.

VII. During the solution of salts in water, a quantity of air is disengaged.—This air was partly contained mechanically in the salt, and partly in the water. That it does not arise entirely from the former source, is proved by varying the experiment in the following manner. Let an ounce or two of the sulphate of soda be put into a vial, and on this let as much water be poured as will completely fill the bottle. The air contained in the pores of the salt will be thus disengaged; but only a small portion of the salt will be dissolved, agreeably to the principle laid down, chap. ii. 7. Let the vial be shaken, and the whole of the salt will disappear; a fresh

portion of air being liberated during its solution.

VIII. During the solution of bodies, the bulk of water changes. -Take a glass globe, furnished with a long narrow neck (commonly termed a matrass, see fig. 4), and put into it an ounce or two Then, add as much water as will fill the globe, of sulphate of soda. and about three 4ths of the neck. This should be done with as little agitation as possible, in order that the salt may not dissolve, till required. Mark, by tying a little thread, or by a scratch with a file, the line where the water stands; and then agitate the matrass. The salt will dissolve; air will be set at liberty; and, during the solution, the water will sink considerably below its level. The contraction of bulk is owing to the diminution of temperature; and, when the water has regained its former temperature, it will also be found, that its bulk is increased by the addition of salt. The late Bishop Watson observed, that water exhibits a manifest augmentation of bulk, by dissolving only the two thousandth part of its weight of salt; a fact sufficiently decisive against that theory, which supposes pores in water capable of receiving saline bodies without an augmentation of volume.

IX: Water has its solvent power increased, by diminishing the pressure of the atmosphere.—Into a Florence flask, put half a pound of sulphate of soda; pour on it barely a pint of water, and apply heat so as to boil the water. The whole of the salt will be dissolved. Boil

<sup>\*</sup> An. de Chim. et Phys. i. 215.

the solution for several minutes pretty strongly, so as to drive out the air; and cork the bottle tightly, immediately on its removal from the fire. To prevent more completely the admission of air, tie the cork over with bladder. As the vessel cools, an imperfect vacuum will be formed over the solution; for the steam which arises during the ebullition expels the air, and takes its place. The steam is condensed again, when the vessel cools. The solution, when perfectly cold, may be shaken without any effect ensuing, so long as the vessel is kept closely stopped; but, on removing the cork and shaking the vessel, the solution will immediately congeal, and heat will be produced. This experiment, besides the principle which it is peculiarly intended to illustrate, exemplifies also the general rule laid down, chap. iii. sect. 2. vi. viz. that caloric is always evolved, during the transition of bodies from a fluid to a solid state; and it furnishes a fact exactly the reverse of that in which cold is produced, or caloric absorbed, during the solution of salts. It is proper, however, to remark that the observations of Dr. Coxe, of Philadelphia\*, have thrown some doubt over the cause of these phenomena, which appears to require farther investigation. From his experiments, the exclusion of air does not seem to be absolutely necessary; for saline solutions continued fluid, if perfectly at rest, through freely exposed to the atmosphere, but immediately became solid when shaken\*. The efficacy of mechanical disturbance in promoting saline crystallization, under circumstances where it has been ascribed to the renewed contact of air with the surface of the solution, is illustrated also by some experiments of Dr. Uret.

X. It is unnecessary to add any thing to what has been already said in a former section, respecting the combination of caloric withwater constituting steam; or to the history of the phenomena attending its conversion into ice; except that, during the latter change, its bulk is enlarged in the proportion of nine to eight, and that, in consequence of this expansion, water, during congelation, is capable of bursting the strongest iron vessels; and becomes specifically lighter. Hence, ice swims always on the surface of the water.

It is remarkable, that this enlargement of the bulk of water begins long before its temperature has descended to the freezing point, viz. at about 40° Fahrenheit. Let a thermometer bulb, and part of its tube, having a wide bore, be filled with water, tinged with a little litmus, which may be introduced by the same means as those already directed for filling with quicksilver. Immerse the thermometer in water of the temperature of 40°; and, when the included water may be supposed to have attained the same degree of heat, remove the instrument successively into water of the temperature of 36° and 32°. At each immersion, the water will rise in the tube. Bring its temperature again to 40°, and it will descend to the same point as before. Place it in water of 50°, and it will again be expanded. Precisely similar effects, therefore, appear to result, in these experiments, from two opposite causes; for the bulk of water is alike increased by reducing or raising its temperature. It is contended,

<sup>\*</sup> Thomson's Annals, vi. 101.

however, by Mr. Dalton, that, in the apparent expansion by a lower temperature, there is a deception, arising from the contraction of the glass, which must lessen the capacity of the bulb, and force the water up the stem. The question is not yet decided; and is still contested by Mr. Dalton against the experiments of Count Rumford and of Dr. Hope. The first mentioned philosopher now contends, that water is of the greatest density at 36° of Fahrenheit, or 4° above its freezing point, and M. Biot infers that the true maximum of density is at 38.16 of Fahr.\*

#### CHAPTER VII.

ON THE CHEMICAL AGENCIES OF COMMON AND GALVANIC ELECTRI-CITY.

THAT branch of natural science which comprehends the phenomena of Galvanism, and the general principles under which they are arranged, is only of recent origin. It was not till the year 1791, that Galvani, an Italian philosopher, being engaged in a course of experiments on animal irritability, observed accidentally the contractions which are excited in the limbs of frogs, by applying a conductor of electricity between a nerve and a muscle. The theory, which he framed to account for this phenomenon, was, that the different parts of an animal are in opposite states of electricity, and that the effect of the metal is merely to restore the equilibrium. analogy, however, was afterwards shown to be without foundation. by Volta, who excited similar contractions by making a connexion between two parts of a nerve, between two muscles, or between two parts of the same muscle; but to produce the effect, two different metals were found to be essential. Hence he was led to infer that, by the contact of different metals, a small quantity of electricity is excited; and to the agency of this electricity, first upon the nerves, and through their mediation on the muscles, he ascribed the phenomena in question.

Several years elapsed, during which the action of galvanic electricity on the animal body, and the discussion of its cause, occupied the attention of philosophers. Early in 1800, the subject took a new turn, in consequence of the discovery by Signor Volta of the Galvanic Pilet; a discovery which has furnished us with new and important instruments of analysis, capable, if any such there are, of leading to a knowledge of the true elements of bodies. From this period, discoveries have multiplied with a rapidity, and to an extent, which surpass any thing before known in the history of science; and the facts are now become so numerous, that an arrangement and classifi-

<sup>\*</sup> Themson's Annals, ix 434.

<sup>†</sup> Philosophical Transactions, 1800; or Philosophical Magazine, vii. 289.

cation of them seem to be preferable to an historical detail in the order of time. The method, which appears to me best calculated to give a distinct view of the subject, is to describe,

I. The construction of galvanic apparatus, and the circumstances

essential to the excitement of this modification of electricity:

II. The facts, which establish its identity with the electricity excited by ordinary processes:

III. The agency of the electric or galvanic fluid in producing

chemical changes:

IV. The theory, by which these changes, in the present state of

our knowledge, are best explained: And

V. The hypotheses, which have been framed to account for the origin of the electricity, excited by galvanic arrangements.

### SECTION I.

### Of the construction of Galvanic Arrangements.

For the excitation of ordinary electricity, it is well known that a class of substances are required, called electrics, by the friction of which the electric fluid is accumulated, and from which it may be collected by a different class of bodies termed non-electrics or conductors. When friction, for example, is applied to the glass cylinder or plate of an electrical machine, that part of the glass, which is in contact with the rubber, attracts the electric fluid from it, as well as from all other conducting bodies, with which the rubber is connected. The glass, regaining instantly its natural state, repels the electric fluid, which is received by the prime conductor, placed for that purpose. All then that is effected, by the action of the machine, is a disturbance of the natural quantity of electricity in bodies, or a transfer of it from some to others, in consequence of which, while the latter acquire a redundance, the former become proportionally deficient in their quantity of electricity.

The conditions necessary to the excitement of galvanic electricity are altogether different; for the class of bodies termed electrics, have now no longer any share in the phenomena. All that is required is the simple contact of different conducting bodies with each other; and it has even been found by Dessaignes that two discs of the same metal, heated to different temperatures, give sufficient electricity to excite contractions in the legs of a frog, prepared for the purpose. Conductors of electricity have been divided into perfect and imperfect, the former comprehending the metals, plumbago and charcoal, the mineral acids, and saline solutions; the latter or imperfect, including water, alcohol and ether, sulphur, oils, resins, me-

tallic oxides, and compounds of chlorine.

The least complicated galvanic arrangement is termed A SIMPLE

GALVANIC CIRCLE. It consists of three conductors, two of which must be of the one class, and one of the other class. In the following Tables, constructed by Sir H. Davy, some different simple circles are arranged in the orders of their powers, the most energetic occupying the highest place.

Table of some Electrical Arrangements, which by combination form Voltaic Batteries composed of two Conductors and one imperfect Conductor.

Zinc, Iron, Tin, Lead, Copper, Silver, Gold, Platina, Charcoal.  Each of these is the positive pole to all the metals below it, and negative with respect to the metals above it in the column.	Solutions of nitric acid, of muriatic acid, of sulphuric acid, of sal ammoniac, of nitre, of other neutral salts.
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Table of some Electrical Arrangements, consisting of one Conductor and imperfect Conductors.

Solution of sulphur and potash, of potash, of soda.	Copper, Silver, Lead, Tin, Zinc, Other Metals, Charcoal.	Nitric acid, Sulphuric acid, Muriatic acid, Any solutions containing acid.
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In explanation of these Tables, Sir H. Davy, observes, that in all cases when the fluid menstrua afford oxygen, those metals, which have the strongest attraction for oxygen, are those which form the positive pole. But when the fluid menstrua afford sulphur to the metals, the metal which, under the existing circumstances has the strongest attraction for sulphur, determines the positive pole. Thus, in a series of copper and iron plates, introduced into a porcelain trough, the cells of which are filled with water or with acid solutions, the iron is positive and the copper negative; but when the cells are filled with solution of sulphuret of potash, the copper is positive and the iron negative. When one metal only is concerned, the surface opposite the acid is negative, and that in contact with solution of alkali and sulphur, or of alkali, is negative\*.

The powers of simple galvanic circles are but feeble; but they may be made sufficiently apparent by the following experiments.

1. When a piece of zinc is laid upon the tongue, and a piece of silver under it, no sensation is excited, so long as the metals are kept apart; but on bringing them into contact, a metallic taste is distinctly perceived. In this case we have an example of the arrangement of two perfect conductors (the metals) with one imperfect one

<sup>\*</sup> El. of Chim. Phil. p. 148.

(the tongue or rather the fluids which it contains.) 'The metallic taste arises, in all probability, from the excitement of a small quantity of electricity by the contact of the metals, and its action on the

nerves of the tongue.

2. A piece of zinc, immersed under water which is freely exposed to the atmosphere, oxidizes very slowly; but when placed in the same situation, in contact with a piece of silver, its oxidation is much more rapid. By immersing iron and silver (also in contact with each other) under diluted muriatic acid, the action of the acid upon the iron is considerably increased; and hydrogen gas is evolved from the water, not only where it is in contact with the iron, but where it touches the silver. These facts explain, why, in the sheathing of ships, it is necessary to use bolts of the same metal which forms the plates; for if two different metals be employed, they both oxidate or rust very speedily, in consequence of their forming, with the water of the ocean, a simple galvanic circle.

## Of compound Galvanic Circles or Batteries.

Galvanic batteries are formed by multiplying those arrangements, which compose simple circles. Thus if plates of zinc and of silver, and pieces of woollen cloth of the same size as the plates, and moistened with water, be piled upon each other (fig. 77. pl. ix.), in the order of zinc, silver, cloth; silver, zinc, cloth; and so on, for twenty or more repetitions, we obtain a galvanic battery, termed, from its discoverer, the *Pile of Volta*. The power of such a combination is sufficient to give a smart shock, as may be felt by grasping in the hands, which should be previously moistened, two metallic rods, and touching with these the upper and lower extremities of the pile. The shock may be renewed at pleasure; until, after a few hours, the activity of the pile begins to abate, and finally ceases altogether.

The metals, composing a galvanic battery, may be more conveniently arranged in the form of a trough, a happy invention of Mr. Cruickshank. In a long and narrow wooden trough, made of baked wood, grooves are cut, opposite to and at the distance of between 3 and 3 of an inch from each other; and into these are let down, and secured by cement, square plates of zinc and copper, previously united together by soldering. (See figs. 37 and 78.) The space, therefore, between each pair of plates, forms a cell for the purpose of containing the liquid, by which the combination is to be made active. The advantage of this contrivance, over the pile, is partly that it is much more easily put in order; but, besides this, it is a more efficient instrument. When constructed in the way which has been described, it affords an example of a galvanic combination of the first kind, formed by two perfect and one imperfect conductor. But it admits of being modified, by cementing, into the grooves, plates of one metal only, and filling the cells, alternately, with two different liquids, as diluted nitric acid and solution of sulphuret of potash. In this case, we have a battery of the second order, formed by the repetition of one perfect and two imperfect conductors. For all

purposes of experiment, the first kind of arrangement is universally

preferred.

Another modification of the apparatus, which may be called the Chain of Cups, was proposed by Volta at the same time that he communicated his invention of the Pile; and, from the recent experiments of Mr. Children\*, it appears to be a very useful and powerful one. It consists of a row of glasses (see fig. 75), such as wine glasses or small tumblers, for the purpose of containing any fluid that may be Into each of these glasses is plunged a plate of zinc and another of copper, each not less than an inch square, which are not to touch each other. The plates of different cups are connected by metallic wires or arcs, in such a manner that the zinc of the first cup communicates with the copper of the second; and the zinc of the second with the copper of the third; and so on through the whole The shock is felt on dipping the fingers of one hand into the fluid of the first cup, and those of the other hand into the last of The superiority of this arrangement consists in both surfaces of each metallic plate being exposed to the action of the liquid; whereas, by soldering the plates together, one of the surfaces of each is protected from the liquid, and contributes nothing to the The common trough has lately been made to combine this advantage, by dividing it into cells, not by plates of metal, but by partitions of glass. Into each of these cells filled with the proper liquid, a plate of each metal is introduced, but not so as to touch each other. A communication is then made, by a metallic arc, between the zinc plate of each cell and the copper one of the next, precisely as in the chain of cups. More lately, the troughs themselves have been made of earthen ware, and the partitions of the same material; the apparatus being completed, in other respects in the manner already described. The plates, also, are now so suspended that when not in use, they may all be lifted out of the cells at once. And it has been recently ascertained that the power of a battery is increased atlleast one half by placing in each cell one zinc and two copper plates, so that each surface of zinc may be opposed to a surface of coppert.

The size of the plates has been varied from one or two inches to several feet. The large battery, described by Mr. Children in the Philosophical Transactions for 1815, consisted of plates each six feet by two feet eight inches, equal to 32 square feet; and the cells were capable of containing about 945 gallons of liquid. For ordinary purposes, plates of two inches square are sufficient; but for the decomposition of several bodies, not less than 100 pairs of plates, each four inches square, are required. The enlargement of the size of the troughs, so as to contain this number, would be extremely inconvenient; and we may therefore combine the power of several troughs,

# Phil. Trans. 1815.

<sup>\*</sup> Philosophical Transactions, 1809, page 32. † See Pepys, in Journal of Science, &c. i. 193.

<sup>§</sup> Some useful information respecting the number and size of plates, adapted to different purposes, is given by Mr. Singer in Nicholson's Journal, xxiv. 174.

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by uniting the zinc end of the one with the copper end of the other, by the intervention of a metallic wire, or by an arc of silver or zinc.

It may be sufficient to add, in general terms, that every combination, which is capable of forming a simple galvanic circle, may, by sufficient repetition, be made to compose a battery. The combinations, also, which are most active in simple circles, are observed to be most efficient in compound ones. The foregoing tables of Sir H. Davy express, therefore, the powers of compound as well as of sim-

ple arrangements.

To construct a battery of the first order, it is essential that a fluid be employed, which exerts a chemical action upon one of the Pure water, entirely deprived of air, appears to be inefficient. In general, indeed, the galvanic effect is, within certain limits, proportional to the rapidity with which the more oxidable metal is acted upon by the intervening fluid. Spring water was found sufficient, in Mr. Children's immense battery, to produce the ignition of platina wire. The fluid generally used is nitric acid, diluted with 20 or 30 times its weight of water. Mr. Children recommends a mixture of three parts fuming nitrous acid, and one sulphuric, diluted with thirty parts of water. Directions, also, respecting the best kind and density of acids, for producing galvanic electricity, are given by Mr. Singer. From his experiments it appears, that acid of different densities is required for different purposes. The best wire melting charge is formed with ten gallons of water, five pounds of nitric acid, and half a pound of muriatic acid.

The power of the apparatus has been found to be increased, when insulated by non-conductors; and when surrounded by an atmosphere of oxygen gas; not sufficiently, however, to make it necessary to resort to either of these expedients in ordinary cases. Oxygen gas disappears in this process, when carried on under a receiver; and after all the oxygen is absorbed, the effect ceases, and is renewed by introducing a fresh portion. A battery, also, which has ceased to be efficient, has its activity renewed by emptying the cells of their liquor, and uncovering the plates. When the cells are filled with diluted nitric acid, the apparatus continues active, even under the exhausted receiver of an air-pump, or in an atmosphere of carbonic acid or nitrogen gases. But if the cells be filled with water only, all action is suspended, by placing it under any of these circumstances. Hence it appears that the oxidation of one or both of the metals, composing the trough, is essential to the excitement of galvanic

electricity.

The electric column may be classed among galvanic arrangements. It was originally contrived by M. de Luc, who formed it of discs of Dutch gilt paper, alternated with similar discs of laminated zinc. These were piled on each other in a dry state, and the instrument, instead of being soon exhausted, like the pile with humid substances, was found to continue active for some years\*. A similar pile may be formed by laying a mixture of very finely powdered zinc with common glue and a little sugar, by means of a brush, on the back of

Nicholson's Journal, vol. xxvi.

Dutch gilt paper; and, when dry, cutting it into discs, which are to be piled on each other\*. Zamboni of Verona has constructed a pile of slips of silver paper, on the unsilvered side of which is spread a layer of black oxide of manganese and honey. These papers are piled on each other to the number of 2000; then covered externally with a coating of shell lac; and enclosed in a hollow brass cylinder. Two of these piles are placed at the distance of four or five inches from each other; and between them is suspended, on a pivot, a light metallic needle, which is attracted alternately to the one pile and the other, so that it moves between them like a pendulum. This instrument has been applied to the measurement of time, by causing it to give motion to the pendulum of a clockt.

### SECTION II.

### On the mutual Relation of Electricity and Galvanism.

Is the influence, it may now be inquired, which is called into action in a way so different from that employed for the excitation of ordinary electricity, identical with it or of a different kind? This question will be decided by examining whether any of those phenomena, which are occasioned by the agency of the electric fluid, are produced also by that of galvanism; and we shall find the following striking resemblances:

1. The sensation, produced by the galvanic shock, is extremely similar to that which is excited by the discharge of a Leyden jar. Both influences, also, are propagated through a number of persons,

without any perceptible interval of time.

2. Those bodies, which are conductors of electricity, are also conductors of the galvanic fluid, as the metals, charcoal, and a variety of liquids. Again, it is not transmitted by glass, sulphur, and the whole class of electrics, which do not convey ordinary electricity. Among liquids, those only are conductors of electricity and galvan-

ism, which contain oxygen as one of their elements.‡

3. The galvanic fluid passes through air and certain other non-conductors, in the form of sparks; accompanied with a snap or report; and, like the electric fluid, it may be made to inflame gunpowder, phosphorus, and mixtures of hydrogen and oxygen gases. It has been found, also, by Mr. Children, that in the Voltaic apparatus there is, what is called in electricity, a striking distance. With a power of 1250 pairs of four inch plates, he found this distance to be one 50th of an inch, the thickness of a plate of air, through which the galvanic discharge is able to pass in the form of a spark. Increasing the number of plates, the striking distance will be greater; and the reverse when it is diminished. It is also increased by rarefying the air, through which the spark is transmitted.

† Phil. Mag. xlv. 261.

Phil. Mag. xlvii. 265.

t Cruickshank, in Nicholson's 4to. Journal, iv. 258.

- 4. The Voltaic apparatus is capable of communicating a charge to a Leyden jar, or even to a battery. If the zinc end of a pile (whether it be uppermost or the contrary) be made to communicate with the inside of a jar, it is charged positively. If circumstances be reversed, and the copper end be similarly connected, the jar is charged negatively\*. The shocks do not differ from those of a jar or battery, charged to the same intensity by a common electrical machine.
- 5. Galvanism, even when excited by a single galvanic circle only (such as a piece of zinc, a similar one of copper, and a piece of cloth moistened with a solution of muriate of ammonia), distinctly affects the gold leaf of the condensing electrometer. If the zinc end be uppermost, and be connected directly with the instrument, the electricity indicated is positive; if the pin of the electrometer touch the copper, the electricity is negative. A pile consisting of sixty combinations produces the effect still more remarkably.

6. The chemical changes produced by galvanic and common electricity, so far as they have hitherto been examined, are precisely similar. These will form the subject of the following section.

### SECTION III.

### On the Chemical Agencies of Electricity and Galvanism.

The effects of the electric or galvanic fluids, in producing chemical decomposition, cannot be described, without introducing to the reader the names of several substances, with which, in the present state of his knowledge, he may be supposed to be unacquainted. This difficulty is unavoidable; for it is impossible to explain the general laws of electro-chemical action, without a variety of particular instances. In general, however, it will be found that a minute acquaintance with the bodies, which are brought in illustration, is by no means essential; and that it is sufficient to consider them as composed simply of two ingredients, which are in opposite electrical states, and are subject to the laws of electrical attraction and repulsion.

The most simple chemical effect, produced alike by the agency of electricity and galvanism, is the *ignition* and *fusion* of *metals*. When a piece of watch-pendulum wire is placed in the circuit of a common electrical battery, containing not less than three or four square feet of coating, at the moment of the discharge the wire becomes red-hot; but continues so only for a few seconds; no longer,

<sup>\*</sup> Cuthbertson's Practical Electricity and Galvanism, p. 261; Volta, in Nicholson's Journal, 8vo. i. 140; Van Marum, in Philosophical Magazine, xii. 162.

<sup>\*</sup> Nicholson, 8vo. i. 139, and ii. 281; Cuthbertson, p. 264.

indeed, than if it had been ignited in any other way\*. The same effect may be produced by making a piece of wire the medium of communication between the opposite extremities of a galvanic trough; but, in this case, the heat continues sensibly longer, than when it is excited by an electrical explosion. Indeed a platina wire may be kept ignited in vacuo, for an unlimited time, by Voltaic electricity. Water, surrounding a wire so placed, may be made to boil briskly.

By means of his large battery, Mr. Children not only ignited wire of considerable thickness; but a bar of platina, th of an inch square and 21 inches long, was ignited, and even fused at one end. The facility of being ignited in the different metals appeared to be inversely proportional to their power of conducting heat. Thus platina, which has the lowest conducting power, was most easily ignited; and silver, which conducts heat better than any other metal,

was ignited with greater difficulty than any of the rest.

It does not appear, that a very powerful combination is required to produce ignition, if the wire be made of proportionately small diameter. Dr. Wollaston has ascertained that a wire  $3\sqrt{6}$ 00 of an inch in diameter may be ignited by a single zinc plate only one inch square, provided each of its surfaces be opposed to a surface of copper or some other metal. The liquor which he employed was a mixture of one measure of sulphuric acid with 50 measures of water. Any farther diminution in the diameter of the wire he found to be unfavourable to the effect, in consequence of the increase of the cooling power of the atmosphere.

When the power of an electrical battery is increased, metallic wires, by transmitting the discharge through them, may be melted and dispersed in the form of smoke, or of an impalpable powder lighter than air. The galvanic discharge, also, is capable of fusing metallic wires; but being less violent, it does not scatter their particles to a distance. Even wire from the most infusible of the metals,

platina, acquires a white heat, and melts into globules.

With a still more powerful electrical battery (one for example containing about 18 square feet) metallic wires are not only melted, but undergo absolute combustion. Lead and tin wire emit a yellow light, and copper and silver a green one. If the experiment be made on wire confined in a glass receiver, which contains a measured quantity of air, the bulk of the air, and its proportion of oxygen, are both found to be diminished. The metals are converted into oxides of different colours; lead, tin, and zinc, into white oxides; platina, gold, silver, and copper, into oxides of a dark colour. The experiment may be pleasingly varied by passing the discharge through wires, stretched over panes of glass or sheets of paper, at a small distance from their surface. The metallic oxide which is produced is forcibly driven into the glass or paper; and produces beautiful figures, varying in colour with the metal employed.

On the quantity of coated surface required for igniting different lengths
of wire, the reader may consult Mr. Cuthbertson's book, p. 161, &c.

<sup>†</sup> Thomson's Annals, vi. 209. ‡ Cuthbertson, p. 199. § Cuthbertson, p. 226; and Wilkinson's Elements of Galvanism, in the 9th plate of which these appearances are represented.

The combustion of metals may be effected, also, by galvanic electricity; but for this purpose the form of very thin leaves is preferable to that of wire. The plates, composing the galvanic trough, should, for this purpose, be not less than four inches square, the larger, indeed, the better; and several troughs should be joined together, so as to form an aggregate of not less than 100 or 150 pairs of plates. The galvanic influence is to be conveyed by wires brought from each extremity of the arrangement, and placed in contact with the opposite surfaces of the leaf. For the protection of the fingers, the wires should be inclosed in glass tubes. When thus exposed, the metals burn, or rather deflagrate, with great brilliancy.

Gold emits a very vivid white light, inclining a little to blue, and leaves an oxide, whose colour verges towards that of mahogany.

Copper presents similar phenomena.

The flame of silver is a vivid green, somewhat like that of a pale emerald, and the light is more intense than that of gold. Lead gives a vivid light of a dilute bluish purple. Tin, a light similar to that of gold; and zinc, a bluish, white flame, fringed with red\*. In all these cases, provided the power be sufficiently strong, the deflagration is kept up, for some time, without intermission.

But a much more remarkable action is exerted by the electric and galvanic fluids, in disuniting the elements of several combinations. One of the first discoveries of the chemical agency of the pile was its power of decomposing water. Two pieces of any metallic wire are thrust through separate corks, which are fitted into the open ends of a glass tube in such a way, that the extremities of the wires, when the corks are in their places, may not be in contact, but may be at the distance from each other of about a quarter of an inch (see fig. 77, a). If the parts of the wire, which project from without the tube, be made to communicate, the one with the zinc or positive end, and the other with the copper or negative end, of a galvanic battery, a remarkable appearance takes place. The wire, connected with the zinc or positive end of the pile or trough, where it is in contact with the water, if of an oxidable metal, is rapidly oxidized; while from the negative wire a stream of small bubbles of gas arises. But if the wires employed be of a metal which is not susceptible of oxidation, such as gold or platina, gas is then extricated from both wires, and, by a simple contrivance, may be separately collected. The apparatus for this purpose is shown by fig. 76, where the wires p and n, instead of being introduced into a straight tube, are inclosed in a syphon, and terminate before they reach the end, in which a small hole is to be ground. When a stream of galvanic electricity is made to act upon water thus confined, oxygen gas is found, at the close of the experiment, in the leg connected with the positive end of the battery, and hydrogen gas in that connected with the negative end; and in the proportions which, by their union, compose water. At an early period of the inquiry, it was found, however, by Mr. Cruick-

<sup>\*</sup> Philosophical Magazine, xi. 284, and xv. 96.

shank, that the water surrounding the positive wire became impregnated with a little acid; and that around the negative wire with a little alkali. If instead of water we employ a metallic solution, the metal is revived round the negative wire n, and no hydrogen gas is liberated.

The gases constituting water, it was afterwards discovered by Sir H. Davy, may be separately produced from two quantities of water, not immediately in contact with each other. The fact is of peculiar importance, from its resemblance to other more recent ones, which have led that distinguished philosopher to the discovery of the general laws of electro-chemical action. Two glass tubes (p and n, pl. ix. fig. 79), about one third of an inch diameter and four inches long, having each a piece of gold wire sealed hermetically into one end and the other end open, were filled with distilled water, and placed inverted in separate glasses filled, also, with that fluid. The two glasses, a and b, were made to communicate, either by dipping the fingers of the right hand into one glass, and those of the left into the the other, or by interposing fresh animal muscle, or a living vegetable, or even moistened thread, as shown at c. The gold wires, projecting from the sealed ends of these tubes, were then connected, the one with the positive, the other with the negative end of the trough. Gas was immediately evolved from both wires. At the close of the experiment, in the tube p, oxygen gas was found; in the negative tube n, hydrogen. The proportions by measure were, as nearly as possible, those which result from the decomposition of water, viz. two of hydrogen to one of oxygen gas\*. Now if these gases arose, as they necessarily must, from the decomposition of the same portion of water, that portion of water must have been contained either in the tube p or in the tube n. In the former case, the hydrogen gas, found after the process in n, must have passed invisibly from p to n, through the intermediate substance c. Or, if the water was decomposed in n, then the reverse process must have happened with respect to the oxygen; and it must have been transmitted, in a like imperceptible manner, from n to p. Facts of this kind, evincing the transference of the elements of a combination, to a considerable distance, through intervening substances, and in a form that escapes the cognizance of our senses, however astonishing, it will appears from the sequel, are sufficiently numerous and well established. It appears, also, from the experiments of Mr. Porrett, that water may be forced, contrary to its gravity, through the compact substance of a bladder, from the positive to the negative wire of a galvanic battery, composed of plates only 11 inch square t.

Different chemical compounds require, for the disunion of their elements, galvanic arrangements of various powers and intensities. The decomposition of water is easily effected by a series of fifty pairs of plates, each one or two inches square. But for those which remain to be described, instruments of much greater power are ne-

cessary.

<sup>\*</sup> Nicholson's Journal, 4to. iv. 276. † Thomson's Annals, viii. 74.

The apparatus, employed in the masterly experiments of Sir H. Davy, which have laid the groundwork of this new field of science. was extremely simple. In cases, where liquid substances were operated upon, he employed occasionally the agate cups p and n, fig. 80, each of which was capable of holding about sixty grains of water. They were connected together, as shown in the figure at a, by the fibres of a peculiar flexible mineral called amianthus; and into each was inserted a platina wire, the bent extremity of which is seen, in each figure, projecting above the cup. When the vessels were in actual use, the wire of p was connected with the zinc or positive end of a powerful galvanic series; and that of n with the copper or negative extremity. For the agate cups two hollow gold cones were occasionally substituted (p and n, fig. 81), the wire projecting from pbeing connected with the positive, and that from n with the negative end of a trough or series of troughs. Solid bodies were submitted to the galvanic influence, either by immersing small pieces of them in the gold cones: or, at other times, by making the cups themselves. of the substance intended to be decomposed. Or if it was desirable to preserve them from contact with water, they were laid on a small insulated dish of platina, with the inferior surface of which, immediately under the substance used, a wire from one end of the battery was connected, while the substance itself was made to communicate by another wire, with the opposite extremity of the apparatus.

When the gold cones were both filled with a solution of sulphate of potash (a salt composed of potash and sulphuric acid), after exposure, during a sufficient time, to a powerful galvanic arrangement, pure potash was found in the negative cone n, and sulphuric acid in the positive cone p. The decomposition was even quite complete; for the liquid in n contained no acid, and that in p no alkali.

The experiment was repeated with several other neutral salts \*; and with the invariable result, that the acid collected in the positive cone, and the alkali in the negative one. Strong solutions, or those in which the salt bore a considerable proportion to the water, were more rapidly acted upon than weak ones. Metallic salts were, also, decomposed. The acid appeared, as before, in the positive cone, and the metal was deposited, sometimes with a little oxide, in the negative one.

Salts, which are either insoluble, or very sparingly soluble, in water, had their elements disunited in the following manner. Cups were constructed of them, precisely resembling the gold cones, which as the salts were hard and compact in their texture, was easily effected. These, after being filled with water, were connected, by platina wires, with the opposite ends of a galvanic battery, the vessels themselves communicating, as before, by means of moistened amianthus. At the conclusion of the experiment, sulphuric acid (when the cups were made of sulphate of lime) was found in the positive cup, and lime water in the negative one. Sulphate of stron-

<sup>•</sup> Minute directions for exhibiting the transfer of acid and alkali, by means of a power not exceeding thirty pairs of two inch plates, are given by Mr. Singer. (Nicholson's Journal, xxiv. 178.)

tites, fluate of lime, and sulphate of barytes, were decomposed, though less easily, by the same expedient. In all these cases the acid element was found at the positive side, and the earthy one at

the negative side, of the arrangement.

These facts evidently point out a transference of the elements of combinations from one electrified vessel or surface to another differently electrified. But the principle is made much more apparent by a little variation of the experiment. Thus, if solution of sulphate of potash be electrified in the positive cone p, water alone being contained in n, after a sufficient continuance of the electrical action p, will be found to contain diluted sulphuric acid; and the potash will be discovered in the water of n. The alkali must necessarily, therefore, have passed, in an imperceptible form, along the connecting amianthus from the vessel p to the vessel n. Reversing the experiment, and filling n with solution of sulphate of potash, the alkali remains in this cone, and the acid is transferred to the opposite side In one experiment, in which nitrate of silver was placed in the positive cup, and pure water in the negative one, the whole of the connecting amianthus was covered with revived silver.

In the farther prosecution of the inquiry, Sir H. Davy succeeded in discovering a still more extraordinary series of facts. When an intermediate vessel (i, fig. 82) was placed between the positive and negative cups p and n, and was connected with both of them by moistened amianthus, it was found that acids may actually be made to pass from n to p, through the intermediate solution in i, without combining with it. Thus, solution of sulphate of potash being put into the negative cup  $\eta$ , solution of pure ammonia into i, and pure water into p, in half an hour sulphuric acid was found in the water of the positive cup, to have reached which it must have been transferred from n through the intermediate solution of ammonia. Muriatic acid, also, from muriate of soda, and nitric acid from nitrate of potash, were transferred from the negative to the positive side through an interposed solution of alkali. And contrariwise, alkalies and metallic oxides were transmitted from the positive to the negative side, through intervening solutions of acids.

It is necessary, however, that the solution, contained in the intermediate vessel i, should not be capable of forming an insoluble compound with the substance intended to be transmitted through it. Thus sulphuric acid, in its passage from sulphate of potash in the negative cup through the vessel i containing a solution of pure barytes, is detained by the barytes, and falls down in the state of an insoluble

compound with that earth.

Budies, the composition of which is considerably more complicated, are, also, decomposed by galvanic electricity. Thus from certain minerals, containing acid and alkaline matter in only very minute proportion, these ingredients are separately developed. salt, for example (a kind of stone which, in one 100 grains, contains only 3½ grains of soda and half a grain of muriatic acid), gave, at the end of ten hours, evident traces of alkali round the negative, and of acid round the positive wire. A slip of glass, also, negatively elec-

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trified in one of the gold cones, had soda detatched from it, and

sustained a loss of weight.

It may now be understood, why, by the agency of galvanism on water, alkali appears at the negative and acid at the positive wire. The fact was, for some time, not a little perplexing to Sir H. Davy; till, at length, he ascertained that all water, however carefully distilled, contains neutral salts in a state of solution. From these impurities, the alkaline and acid elements are separated, agreeably to a law which has already been explained. In the same way, also, the muriatic acid and alkali are accounted for, which some chemists have obtained by galvanizing what was before considered as pure water; a fact which has been urged in proof of the synthetical production of both those bodies. Absolutely pure water, it has been demonstrated by Sir H. Davy, yields nothing but hydrogen and oxygen gases.

All the effects of galvanic arrangements, in producing chemical decompositions, it has been found, may be obtained by ordinary electricity. Its adaptation to the purpose was first successfully attempted by Dr. Wollaston\*. The appratus, which he employed, was similar to that already represented (fig. 77, a), excepting that the wires, instead of being exposed to the fluid, contained in the tube, throughout their whole length, were covered with wax, and the points only were laid bare. Or (what was found to answer still better) the wires were inclosed in capillary tubes, which were sealed at their extremities, and then ground away, till the points alone were exposed. The conducting wires, thus arranged, were then introduced into a tube, or other vessel containing the liquid to be operated on, and were connected, the one with the positive, the other with the negative, conductor of an electrical machine, disposed for positive and negative electricity. When solution of sulphate of copper was thus electrized, the metal was revived round the negative pole. On reversing the apparatus, the copper was re-dissolved, and appeared again at the other wire, now rendered negative.

When gold wires from , 185 to 150 to of an inch in diameter, thus inclosed, were made to transmit electricity, a succession of sparks afforded a current of gas from water. When a solution of gold in nitro-muriatic acid was passed through the capillary tube; the tube then heated to drive off the acid; and afterwards melted and drawn out, it was found that the mere current of electricity, without sparks,

envolved gas from water.

Sir H. Davy has since proved that by a similar apparatus, solution of sulphate is decomposed, potash appearing at the negative, and sulphuric acid at the positive pole‡.

<sup>\*</sup> Philosophical Transactions, 1801.

<sup>†</sup> See Cuthbertson's Practical Electricity. ‡ Philosophical Transactions, 1806.

#### SECTION IV.

Theory of the Changes produced by Galvanie Electricity.

A fact of considerable importance in explaining the phenomena that form the subject of the last section was discovered several years ago by Mr Bennett, and has since been confirmed by the experiments Different bodies, it is found acquire, when of Volta and Davy. brought into contact either by the whole surfaces or by a single point, different states with respect to their quantities of electricity. best method of performing the experiment is to take two discs or plates, the one of copper, the other of zinc, each about four inches diameter, and furnished with an insulating glass handle; to apply them for an instant to each other by their flat faces; and afterwards, to bring them separately into contact with the insulated plate of the condensing electrometer. The instrument indicates, by the divergence of its gold leaves, the electricity acquired by each of the plates, which in the zinc plate is shown to be positive, in the copper plate negative\*.

It had been established, also, by Sir H. Davy, in 1801, that when a galvanic arrangement of the second kind is constructed, by alternating metallic plates with strata of different fluids, alkaline solutions always receive electricity from the metal, and acids on the contrary transmit it to the metal. When an arrangement, for example, is made of water, tin, and solution of potash, the current of electricity is from the tin to the alkali. But, in an arrangement of nitric acid, tin, and water, the circulation of electricity is from the acid to the tin. If then the alkali, after having acquired electricity fom the metal, could be suddenly separated from the combination, there can be no doubt that it would be found in a positive state. For the contrary reason, the acid having given electricity to the metal, must, if

it could be detached, be found negative.

Still more satisfactory evidence has been since obtained of the electrical state of the acids and alkalies, by examining what kind of electricity they impart to an insulated metallic plate. Various dry acids, being touched on an extensive surface by a plate of copper insulated by a glass handle, the copper was found after contact to have become positively electrified, and the acid negatively. On the contrary, making the experiments with dry earths in a similar manner, the metal became negative. The alkalies gave less distinct results, owing to their attraction for moisture. Bodies, moreover, possessing opposite electrical energies towards one and the same body, are found to possess them with regard to each other. Thus when lime and oxalic acid were brought into contact, the earth was found to be positive, and the acid negative. Sulphur appears to be in the positive

<sup>\*</sup> Volta, in Nicholson's Journal, 8vo. i. 136. Wilkinson, ii. 40, 50, 131. Cuthbertson, 267.

state. Oxygen, judging from those compounds in which it is looselv combined, is negative; and hydrogen, by the same test, positive.

Now, if the common laws of electrical attraction and repulsion operate, as there is every reason to believe they must, among bodies so constituted, it will follow that hydrogen, the alkalies, metals, and oxides, being positively electrified, will be repelled by surfaces which are in the same state of electricity as themselves, and will be attracted by surfaces that are negatively electrified. And, contrariwise, oxygen, and the acids (in consequence of the oxygen they contain), being in a negative state, will be attracted by positive surfa-

ces and repelled by negative ones.

To apply this theory to the simplest possible case, the decomposition of water, the hygrogen of this compound, being itself positively electrified, is repelled by the positive wire and attracted by the negative one; while, on the contrary, oxygen, being negative, is repelled by the negative wire, and attracted by the positive one. The flame of a candle, which consists chiefly of ignited charcoal, when placed between a positive and negative surface, bends towards the latter; but the flame of phosphorus, consisting chiefly of acid matter, when similarly placed takes a direction towards the positive surface. In the case of neutral salts, the negative acid is attracted by the positive wire; and the positively electrified alkali by the negative wire.

Thus then a power has been discovered, superior in its energy to chemical affinity, and capable either of counteracting it, or of modifying it according to circumstances. The chemical attraction between two bodies may be destroyed, by giving one of them an electric state opposite to its natural one; or the tendency to union may

be increased, by exalting the natural electric energies.

All bodies, indeed, that combine chemically, so far as they have hitherto been examined, have been found to possess opposite states of electricity. Thus copper and zinc are in opposite states to each other; so are gold and mercury; sulphur and metals, acids and alkalies. By bringing two bodies into the same electrical state, which were before capable of union, we destroy their tendency to combination. Thus zinc or iron, when negatively electrified, will not unite with oxygen. Even after combination, it is thought by Sir H. Davy, not improbable, that bodies may still retain their peculiar states of electricity. If oxygen prevail, in any compound, over the combustible or positive base, the compound is negative, as in certain metallic oxides. But the combustible ingredient may be in such proportion, as to predominate, and to give to the compound a positive energy. When precise neutralization is attained, bodies that had before exhibited electrical effects are deprived of this property.

It is an interesting question, but one which can scarcely be determined in the present state of the science, whether the power of electrical attraction and repulsion be identical, as Sir H. Davy has suggested, with chemical affinity, or whether it may not rather be considered, like caloric, as a distinct force, which only modifies that of chemical attraction. On the former hypothesis, two bodies, which are naturally in opposite electrical states, may have these

states sufficiently exalted, to give them an attractive force superior to the cohesive affinity opposed to their union: and a combination will take place, which will be more or less energetic, as the opposed forces are more or less equally balanced. Again, when two bodies, repellent of each other, act upon a third with different degrees of the same electrical energy, the combination will be determined by the degree. Or, if bodies, having different degrees of the same eccltrical energy with respect to a third, have likewise different energies with respect to each other, there may be such a balance of attracting and repelling forces as to produce a triple compound.

This hypothesis, it is remarked by Sir H. Davy, agrees extremely well with the influence of mass, which has been so well illustrated by Berthollet; for many particles, acting feebly, may be equal in effect to fewer acting more powerfully. Nor is it at all contradictory to the observed influence of caloric over chemical union; for an increase of temperature, while it gives greater freedom of motion to the particles of bodies, exalts all their electrical energies. This Sir H. Davy ascertained with respect to an insulated plate of copper and another of sulphur, when heated below 212° Fahrenheit; and at a still higher temperature these bodies, as is well known, combine with the extrication of heat and light, and the usual accompaniments of intense chemical action.

On the supposition that electricity is a force which only modifies the action of chemical affinity, we may regard it, when it promotes combination, as producing this effect by counteracting cohesive attraction. When it impedes combinations, or destroys those which are already formed, it probably acts as a force co-operating with

elasticity.

#### SECTION V.

# Theory of the Action of the Galvanic Pile.

Two theories have been framed to account for the phenomena of the Galvanic Pile, and of all similar arrangements. The first, originating with Volta, was suggested by the fact, which may be considered, indeed, as fundamental to it—that electricity is excited by the mere contact of different metals. When a plate of copper and another of zinc are made to touch by their flat surfaces, as was stated in the last section, the zinc, after separation, exhibits positive electricity, and the copper negative. It is natural, therefore, to conclude that a certain quantity of electricity has moved from the copper to the zinc. On trying other metals, Volta found that similar phenomena take place; and by a series of experiments he was led to arrange the powers in the following order, it being understood that the first gives up its electricity to the second; the second to the third; the third to the fourth, and so on.

Silver. Copper. Iron. Tin. Lead. Zinc.

The metals, then, have been denominated by Volta, from this property, motors of electricity; and the process, which takes place, electro-motion, a term since sanctioned by the adoption of it by Sir

H. Davv.

It is on this transerence of electricity from one body to another by simple contact, that Volta explains the action of the instrument discovered by himself, and of all similar arrangements. The iterposed fluids, on his hypothesis, have no effect as chemical agents in producing the phenomena, and act entirely as conductors of electricity. Without disputing, however, the accuracy or value of the facts which suggested his theory, it is sufficient for its refutation that it is irreconcileable with other phenomena; and especially with the observation, that the chemical agency of the liquids, on the more oxidizable metal of galvanic arrangements, is essential to their sustained activity. It has been proved, indeed, that the phenomena begin and terminate with the oxidation; and that the energy of the pile bears a pretty accurate proportion to the rapidity of the process. Hence it seems, on first view, an obvious inference, that the oxidation of the metal is the primary cause of the evolution of electricity in galvanic arrangements. It has been proved, however, that it is not necessary to the excitement of electricity, that the amalgam should be oxidated; for the machine continues to act when inclosed in hydrogen gas or carbonic acid; and the electric column of M. de. Luc is composed of dry substances. Even in this instrument, the oxidation of the metals appears to be essential to its activity, for when the column is hermetically confined in a given portion of air, the phenomena cease in time, in consequence of the loss of its oxygen.

But though the chemical agency of the fluids which are employed is now admitted, on all hands, to be essential to the excitement of this kind of electiricty, yet is by no means universally agreed that we are to consider it as the first in the order of phenomena. It has been suggested by Sir A. Davy, as a correction of the theory of Volta, that the electro-motion occasioned by the contact of metals, is the primary cause of the chemical changes; and that the changes are in no other way efficient, than as they restore the electric equilibrium. To explain this, let us suppose that in any three pairs of plates of a galvanic trough, the zinc plates z 1, z 2, z 3, (fig. 78), are in the state of positive, and the copper plates c1, c2, c3, in that of negative electricity. The liquid, in any cell after the first, will be in contact, on the one side, with positively electrified zinc, and on the other with negatively electrified copper. And if the elements composing the fluid be themselves in different states of electricity, the negatively electrified elements will be attracted by the zinc, and the positively electrified element by the copper. Thus when solution of muriate of soda in water is the fluid, the oxygen and the acid will pass to the zinc or positive plate, and the alkali to the copper one; while the hydrogen, having no affinity for copper, escapes. The electric equilibrium will be restored, but only for a moment; for, as the interposed fluid is but a very imperfect conductor of electricity, the zinc and copper plates will, by their electromotive power, again assume their states of opposite electricity; and these changes will go on, as long as any muriate of soda remains undecomposed. In a Voltaic arrangement, therefore, the electrical energies of the metals with respect to each other, or to the substances disolved in water, are the causes disturbing the equilibrium; and the chemical changes are the causes that restore it.

No theory of the galvanic pile, however, can be considered as complete, that does not account for the accumulation of electricity at the zinc end of the apparatus. On the theory that the oxidation of the zinc is the source of the evolved electricity, the fact has been ingeniously explained by Dr. Bostock. He takes it for granted that the electric fluid has an affinity for hydrogen; and supposes that the electricity, evolved at the surface of the first zinc plate, is carried, united to hydrogen, through the fluid of the cell to the opposite copper plate. Here the hydrogen and electricity separate; the former flies off in the state of gas, and the latter passes outwards to the next zinc plate. Being in some degree accumulated in this plate, it is disengaged by the action of the fluid in a more concentrated state than before. And in the same manner, by multiplying the number of pairs, it may be made to exit, in the zinc end of

the pile, in any assignable degree of intensity.

On this theory, the electricity evolve is actually generated by the chemical action of the interposed fluids on every zinc plate of the series; and its accumulation is the aggregate of what is thus evolved. The concentration, which takes place at the zinc end of the arrangement admits, however, of being explained by the hypothesis of Volta, especially as modified by Sir H. Davy. Taking the first cell as an example, the fluid interposed between the positive zinc plate z 1, fig. 78, and negative copper plate c 2, being itself a conductor of electricity, must in time produce an equilibrium between these two plates; but this can only be done by the passage of a certain quantity of electricity across the fluid. The absolute quantity of electricity will, therefore, be diminished in the first pair, and increased in the second. In like manner, the second zinc plate will give up part of its electricity to the third copper plate, and the second pair of plates will be deprived of part of its electricity. The electricity, thus lost by the second pair, it will regain from the first pair of plates. By multiplying, in this way, the number of plates, every successive pair, as we advance in the series, has a tendency to dimish the quantity of electricity in the first; and to have its own state of electricity proportionally exalted.

When a communication is made between two extremities of a series, for example between  $x^3$  or its contiguous cell, and  $c^1$ , the

opposite electricities tend to an equilibrium. The third pair gives up a share of its electricity to the first; and the intermediate pair, being placed between equal forces, remains in equilibrio. Hence, in every galvanic arrangement, there is a pair of plates at the centre, which is in its natural state of electricity. The effect of such a communication must necessarily be to reduce the pile to a state of inactivity, if there did not still exist some cause sufficient to destroy the equilibrium. On the hypothesis of Volta, this can be nothing else than the property of electro-motion in the metals, which originally produced its disturbance.

Such are the hypotheses that have been framed to explain the phenomena of the Voltaic pile. In the present state of the science, neither of them is entitled to be received as altogether satisfactory; and I have stated them rather with the view of exciting than of satisfying inquiry\*. On the theory of galvanic electricity, it only remains to point out its difference from the electricity developed by ordinary processes; and to explain the different effects, which are produced by varying the size of the plates in galvanic arrangements.

Though the identity of common and galvanic electricity appears to be sufficiently established, yet in some of their phenomena, which have already been described, there is a considerable difference. To explain these, it was long ago suggested by Mr. Nicholson', that the electricity, excited by the common machine, is developed in much smaller quantity, but in a higher state of concentration or intensity than the electricity of galvanism. Hence, its velocity is much more rapid; and hence it readily passes through plates of air and other non-conductors, that are scarcely permeable by galvanic electricity. By virtue of the same property it disperses the metals in the form of smoke; while the utmost effect of a Voltaic arrangement is to melt them into globules. By doubling the quantity of galvanic electricity, also, we ignite only a double length of metallic wire, and the ignition is more permanent; but the intensity of common electricity is such, that by doubling its quantity we ignite four times the length of wire, and the effect is little more than momentaryt.

The comparative quantities of electricity evolved by the common machine and by a Voltaic apparatus, have been made a subject of calculation by Mr. Nicholson. A pile consisting of 100 half crowns, with the same number of pieces of zinc, produces, he found, 200 times more electricity than can be obtained, in an equal time, from a 24 inch plate machine in constant action. Van Marum has, also, observed that a single contact of a Leyden jar or battery with a Vol-

<sup>\*</sup> The reader, who wishes to pursue the subject, may consult an essay by the author, in Nicholson's Journal, xxxv. 259; M. De Luc's papers, xxxi. 271, and xxxvi. 97; Mr. Singer on the Electrical Column, xxxvi. 373, and his work on Galvanic Electricity; Dr. Bostock's Essay in Thomson's Annals, iii. 32; Sir H. Davy's chapter on Electrical Attraction and Repulsion, in his Elements of Chim. Philos, p, 125, and the 1st, vol. of Gay Lussac and Thenard's Recherches.

<sup>†</sup> See his Journal, 4to. iv. 244.

<sup>‡</sup> Cuthbertson, p. 278.

taic pile charges it to the same degree, as six contacts with the

prime conductor of a powerful machine.

It might naturally be expected that a proportion would be observed between the quantity of surface composing galvanic arrangements, and their power of action; and such, with some limitation, is the fact. With plates of the same size, the effect, generally speaking, is proportional to the number. But by enlarging the size, without increasing the number, neither the shock nor the power of decomposing water and other imperfect conductors, is proportionally increased. A remarkable proof of this is, that Mr. Children's great battery of 20 double plates, 4 feet by 2, had no more effect on the human body, or in decomposing water, than a battery containing the same number of small plates. On the contrary, to obtain a great increase of effect in the combustion of metals, it is necessary to enlarge considerably the size of the plates. Thus 100 plates of four inches square produce, in this way, an incomparably greater effect, than the same surface divided into four times the number.

The effect of multiplying the number of plates, it has already been observed, is, that we obtain electricity of a higher intensity, and it was supposed by Volta\* that the proportion is, as nearly as can be judged, an arithmetical one. If, for example, we have a certain intensity with 20 pairs, it should be doubled by 40, trebled by 60, and so on. It has been shown, however, by Sir H. Davyt, that by increasing the number of plates, the quantity of gas, evolved from water, were nearly as the squares of the numbers. By a sufficient increase, the most astonishing effects may be produced. Thus the combination belonging to the Royal Institution, which contains 2000 double plates, each having a surface of 32 square inches, when in action, melts platinum, as easily as wax is melted by a candle, and fuses quartz, the sapphire, lime, and magnesia. By enlarging the size, without increasing the number, it has also been shown that we gain, not in intensity, which remains exactly the same, but in quantity. Now, for the combustion of metals what we principally want is a large quantity of electricity; for as they are perfect conductors, it finds a ready passage through them even when of low intensity. On the contrary, to find its way through fluids and other imperfect conductors, it must be evolved in a high state of concentration. The facts, therefore, accord sufficiently well with the explanation, to entitle it to be received as a probable hypothesis.

<sup>Nicholson's Journal, 8vo. i. 139.
† Elements of Chem. Philos. p. 155.</sup> 

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### CHAPTER VIII.

#### · ALKALIES.

The alkalies, in their pure state, are the products of chemical operations, which will be described in the sequel. They are distinguished by the following

### General Qualities.

The properties, common to all the alkalies, may be shown by those of a solution of pure potash.

(a) The alkalies change vegetable blue colours, as that of an in-

fusion of violets to green.

(b) They have an acrid and peculiar taste.

(c) They serve as the intermedia between oils and water.

(d) They corrode woollen cloth; and, if the solution be sufficiently strong, reduce it to the form of a jelly.

(e) They are readily soluble in water.

(f) The fixed alkalies unite with water, and form solid hydrates.

### SECTION I.

# Pure Potash and pure Soda.

# ART. I .- Their Preparation and General Qualities.

To prepare pure potash, dissolve any quantity of American or Dantzic pearlash in twice its weight of boiling water, and add the solution, while hot, to an equal weight of fresh quicklime, slaked with six times its weight of hot water. Boil the mixture in an iron kettle, and continue stirring during half an hour. Then separate the liquid alkali, either by filtering through calico or by subsidence; and boil it to dryness in a silver dish. Pour, on the dry mass, as much pure alcohol as is required to dissolve it; put the solution into a bottle, and let the insoluble part settle to the bottom. Then decant the alcoholic solution of potash; and distil off the alcohol in an alembic\* of pure silver, furnished with a glass head. Pour the alkali, when in fusion, upon a silver dish, and, when cold, break it into pieces, and preserve it in a well-stopped bottle. If the distillation of the alcohol be not carried so far the alkali will shoot, on cooling, into regular crystals, containing 53 per cent. of water.

From the electro-chemical researches of Sir H. Davy, it appears that potash is not completely deprived of carbonic acid, by any pro-

<sup>\*</sup> The figure of an alembic may be seen in pl. i. fig. 2.

cess hitherto employed for its preparation\*. Probably the method suggested by Darcet, of removing the last portions of carbonic acid from an alkaline liquor by solution of barytes, after the full action of lime, would be found effectual.

In the same mode may pure soda be prepared, substituting the

carbonate of soda for the pearlash.

These alkalies have the following properties:

(a) They powerfully attract moisture from the atmosphere, or

deliquiate.

(b) They readily dissolve in water, and produce heat during their solution, if the fused alkalies be employed; but the crystallized alkalies generate cold, when dissolved.

(c) They are not volatilized by a moderate heat, and hence have

been called fixed alkalies.

(d) When melted with silex, in proper proportions and by a sufficient heat, they form glass.

## Hydrated Alkalies.

It is necessary to observe that the alkalies, even after being kept some time in fusion, contain a quantity of water in the state of combination; in other words, are hydrates. This discovery appears to be due to Darcet, who has established his claim very satisfactorilyt. Various proportions of water and alkali have been assigned to these compounds. Berthollet, in the 2d vol. of the Mémoires d'Arcueil, states that 100 parts of solid potash contain 13½ parts of water; but Sir H. Davy‡ has raised it as high as from 17 to 19 per cent.; and Gay Lussac and Thenard allow about one fifth of water in solid potash. One possible source of fallacy is, that if the alkali contain soda, the proportion of water will appear too great; because that alkali combines with more water than potash. If, as Mr. Dalton suspects, the hydrate of potash be a compound of 1 atom of potash + 1 atom of water, its atom should weigh 56.5; and it ought to be composed of

84.9 potash } 15.1 water }	or	{ 84 { 16
100		100

And it is remarkable, that according to the theoretical view of Berzelius, potash, to become a hydrate, requires a quantity of water containing precisely as much oxygen as exists in the alkali united with potassium; that is, 100 parts of the hydrate should contain 16,15 of water §.

There is also considerable difference in the statements respecting Hydrate of Soda. Berard makes it contain 18.86 per cent. of wa-

en la facilità de la companya de la

<sup>\*</sup> Philosophical Transactions, 1808, p. 355.

<sup>† 71</sup> Ann. de Chim. p. 202.

Elements, p. 326.

<sup>§ 82</sup> Ann. de Chim. p. 11.

ter; Darcet 28; and Sir H. Davy from 23 to 25\*. If the atom of soda weigh, as Mr. Dalton supposes, 28, and if the hydrate consist of 1 atom of soda + 1 atom of water, the atom of hydrate of soda should weigh 36.5, and the hydrate should be composed of

76.7 soda · 23.3 water

100.

In these instances, the theoretical view, and the best practical result, confirm each other.

It is often of importance to know the quantity of real alkali, contained in solutions of different specific gravities. The following tables have been constructed by Mr. Dalton from his own experiments, cond ted with great attention to accuracy.

 Table of the Quantity of Real Potash in watery Solutions of different Specific Gravities.

Atoms of Potash Water.	Potash per cent. by weight.	Potash per cent. by measure.	Specific Gravity.	Congealing point.	Beiling point.
1 + 0	100	240	2.4	unknown.	unknown.
1 + 1	84	185	2.2	1000°	red heat.
1 + 2	72.4	145	2.0	500°	· 600°
1 + 3	63.6	119	1.88	- 340°	420°
1 + 4	5 <b>6.</b> 8	101	1.78	220°	360°
1 + 5	51.2	86	1.68	150°	320°
1 + 6	46.7	75	1.60	100°	290°
1 + 7	42.9	65	1.52	70°	276°
1 + 8	39.6	58	1.47	50°	265°
$1 \dotplus 9$	36.8	53	1.44	40°	255°
1 +10	34.4	49	1.42	1	246°
_	32.4	45	1.39	1 '	240°
	29.4	40	1.36		234°
•	26.3	35	1.33		229°
	23.4	30	1.28	1	2240
	19.5	25	1.23	1	220°
	16.2	20	1.19		218°
	13	15	1.15		215°
	9.5	10	1.11	I	214°
	4.7	5	1.06		213°

Phil. Trans. 1811.

## 2. Table of the Quantity of Real Soda in watery Solutions of different Specific Gravities.

	·			· · · · · · · · · · · · · · · · · · ·	
Atoms of Soda Water.	Soda per cent. by weight.	Soda per cent. by measure.	Specific Gravity.	Congealing point.	Boiling point.
1 + 0	100	230?	2.30?	1000o	unknown
1 + 1	77.8	156	2.	5000	red hot.
1 + 2	63.6	118	1.85	250°	600°
1 + 3	53.8	93	1.72	150°	400°
1 + 4	46.6	76	1.63	800	300°
1 + 5	41.2	64	1.56	1 ' '	280°
1+6	36.8	55.	1.50		265°
•	34	50	1.47	Į	255°
	31	45	1.44		248°
	<b>£</b> 9	40	1.40	I	242°
	26	35	1.36	ł	235°
	23	30	1.32	•	228°
	19	25	1.29		224°
	16`	20	1.23		220°
	13	15	1.18	]	217°
	9	10	1.12	1	214°
	4.7	5	1.06		213°

## ART. 2.—Analysis of the two fixed Alkalies.

Though it had long been conjectured\* that the fixed alkalies are not simple or elementary bodies, yet no distinct evidence had been obtained of their nature, until, in the year 1807, it was furnished by the splendid discoveries of Sir H. Davy. From the facts which have been stated in a former section respecting the powers of electrical decomposition, it appeared to that philosopher a natural inference, that the same powers, applied in a state of the highest possible intensity, might disunite the elements of some bodies, which had resisted all other instruments of analysis. If potash, for example, were an oxide, composed of oxygen united to an inflammable base, it seemed to him probable, that when subjected to the action of opposite electricities, the oxygen would be attracted by the positive wire and repelled by the negative. At the same time, the reverse process might be expected to take place with respect to the combustible base, the appearance of which might be looked for at the negative pole.

In his first experiments, Sir H. Davy failed to effect the decomposition of potash, owing to his employing the alkali in a state of aqueous solution, and to the consequent expenditure of the electrical energy in the mere decomposition of water. In his next trials, the alkali was liquified by heat in a platinum dish, the outer surface of which immediately under the alkali, was connected with the zinc

<sup>\*</sup> See Philosophical Magazine, xxxii, 18, 62.

or positive end of a battery consisting of 100 pairs of plates each six inches square. In this state the potash was touched with a platinum wire proceeding from the copper or negative end of the battery; when instantly a most intense light was exhibited at the negative wire, and a column of flame arose from the point of contact, evidently owing to the development of combustible matter. The results of the experiment could not, however, be collected, but were

consumed immediately on being formed.

The chief difficulty in subjecting potash to electrical action is, that in a perfectly dry state it is a complete non-conductor of electricity. When rendered, however, in the least degree moist by breathing on it, it readily undergoes fusion and decomposition, by the application of strong electrical powers. For this purpose, a piece of potash, weighing from 60 to 70 grains, may be placed on a small insulated plate of platinum, and may be connected, in the way already described, with the opposite end of a powerful electrical battery, containing not less than 100 pairs of six inch plates. On establishing the connexion, the potash will fuse at both places where it is in contact with the platinum. A violent effervescence will be seen at the upper surface, arising, as Sir H. Davy has ascertained, from the escape of oxygen gas. At the lower or negative surface, no gas will be liberated; but small bubbles will appear, having a high metallic lustre, and being precisely similar in visible characters to quicksil-Some of these globules burn with an explosion and bright flame; while others are merely tarnished, and are protected from farther change by a white film, which forms on their surface\*.

This production of metallic globules is entirely independent of the action of the atmosphere; for Sir H. Davy finds that they may

be produced in vacuo.

Pure soda gives similar results; but its decomposition demands a greater intensity of action. The quantity of soda should not exceed 15 or 20 grains: and the distance between the platina surfaces must be reduced from  $\frac{1}{4}$  to  $\frac{1}{8}$  or  $\frac{1}{10}$  of an inch. The metal from soda does not, like that from potash, continue fluid at the temperature of the atmosphere; but speedily becomes solid, and bears a considerable resemblance to silver. When the electrical power is much increased, globules of the metal fly with great velocity through the air, in a state of vivid combustion, producing beautiful jets of fire.

To preserve these new substances, it is necessary to immerse them immediately in pure naphtha, a fluid which will be described in a subsequent part of the work. If they are exposed to the atmosphere, they are rapidly converted back again into the state of pure potash or pure soda. To prevent their oxidation still more effectually, Mr. Pepys has proposed to produce them under naphtha; and has contrived an ingenious apparatus for this purpose, which is described in the 31st volume of the Philosophical Magazine, page 241.

When the globules, obtained either from potash or soda, are ex-

<sup>\*</sup> For the repetition of this experiment, very useful practical directions may be found in a paper by Mr. Singer—Nicholson's Journal, xxiv. 174.

posed to the action of air over mercury in graduated glass tubes, an absorption of oxygen happens; and a crust of alkali is formed on the surface, which defends the interior from farther charge. When heat is applied to the globules similarly confined, a rapid combustion ensues, attended with a brilliant white flame. The globules are found, after the experiment, converted into a white substance; which is potash when we have used those from potash, and soda when the globules from soda have been employed. In this process, oxygen is absorbed, and the weight of the alkali produced is found to exceed that of the globules consumed.

When either of these substances is thrown into water, a rapid disengagement of hydrogen gas takes place; and the oxygen of the

water, uniting with the globules, regenerates alkali.

Nothing then can be more satisfactory than the evidence, furnished by these experiments, of the nature of the fixed alkalies. By the powerful agency of opposite electricities, each of them is resolved into oxygen and a peculiar base\*. This base, like other combustible bodies, is repelled by positively electrified surfaces, and attracted by negative ones; and hence its own natural state of electricity must necessarily be positive. Again, by uniting with oxygen, these bases are once more changed into alkali, either slowly at ordinary temperatures; or with heat and light, if their temperatures be raised. We have evidence, therefore, both of analysis and synthesis, that each of the fixed alkalies is a compound of oxygen with a peculiar inflammable basis.

But in what class of combustible bodies are we to arrange the alkaline bases? Some properties, common to both, have influenced Sir H. Davy to place them among the metals, with which they agree in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination. The only property, which can be urged against this arrangement, is their extreme levity, which even exceeds that of water. But when we compare the differences which exist among the metals themselves, this will scarcely be considered as a valid objection. Tellurium, for example, which no chemist hesitates to consider as a metal, is only about six times heavier than the base of soda, while it is four times lighter than platinum; thus forming a sort of link between the old metals and the bases of the alkalies.

In giving names to the alkaline bases, Sir H. Davy has adopted that termination, which, by common consent; has been applied to other newly discovered metals, and which, though originally Latin, is now naturalized in our language. The base of potash he has called potassium, and the base of soda sodium; and these names have met with universal acceptation among chemical philosophers.

It is not, however, by electrical means only that the decomposition of the fixed alkalies has been accomplished. Soon after Sir H. Davy's discoveries were known at Paris, Messrs. Gay, Lussac, and

<sup>\*</sup> The proportions of oxygen and base in each will be found at the end of the articles Potassium and Sodium.

Thenard\* succeeded in their attempts to decompose both the fixed alkalies, without the aid of a Voltaic apparatus, and merely by the intervention of chemical affinities. Their process, though it affords the alkaline bases of less purity, yields them in much larger quantity than the electrical analysis, viz. to the amount of nearly 400 grains by one operation. It consists in bringing the alkalies into contact with intensely heated iron, which, at this temperature, attracts oxy-

gen more strongly than the alkaline base retains it.

The apparatus, used for obtaining potassium, differs very little from that which is commonly employed to decompose water by means of iron t. It consists of a common gun-barrel curved and drawn out, at one end, to rather a smaller diameter, as represented in the 9th plate, fig. 83, c. To one end is adapted an iron tube a, of the capacity of two cubic inches, for containing the potash. At the bottom of this tube is a small hole through which the potash gradually flows. To the opposite end of the gun-barrel a tube of safety e is to be cemented; and into this a sufficient quantity poured, either of mercury or naphtha. Into the gun-barrel, 21 parts of very clean iron turnings are to be introduced, and pushed on to the bent part c. The tube, carefully luted, is then to be placed in a small furnace nine or ten inches in diameter, and provided with a pair of double blast bellows, the pipe from which is shown at f. The next step is to insert the tube a in its place, after having put into it 12 parts of pure potash, deprived of as much water as possible by previous fusion. whole apparatus should be perfectly dry, clean, and impervious to

A strong heat is now to be excited in the furnace d; and while this is doing, the tube containing the potash, as well as the opposite end of the barrel, should be kept cool by ice. When the barrel has attained a white heat, the potash in a may be melted by a small portable furnace. It will then flow, through the small hole, upon the iron turnings. A considerable quantity of hydrogen gas will be evolved by the decomposition of that portion of water, which the potash retains even after fusion, and which has been shown to exceed When the production of this gas slackens, we may 13 per cent. remove the small furnace from beneath the tube a, and increase the heat in the furnace d, in order to restore to the iron turnings at c the temperature proper for decomposing more potash. These operations may be repeated, alternately, till no more gas is produced; but last of all, the heat in the furnace should be strongly raised, in order to drive off some of the potassium. which strongly adheres to the iron turnings.

Annales de Chimie, lxv. 325; or Memoires de Arcueil, ii. 299.

<sup>†</sup> Hachette, in Philosophical Magazine, xxxii. 89; and Mr. E. Davy, ditto, page 276. Ample details respecting the preparation of potassium are, also, given in the first volume of Gay Lussac and Thenard's Physico-Chimiques, and a simple and ingenious apparatus for procuring this metal, is described; by Mr. Tennant in the Phil. Trans. for 1814. See also Mr. Brande's directions in the Supplement now publishing to the Encyclop. Britan. iii. 36.

When the furnace is quite cold, the safety tube e is to be removed, and its place supplied by an iron plug. If the end of the gun-barrel, projecting from this side of the furnace, has been kept carefully cooled during the experiment, the metal will be found adhering to it, in the form of brilliant laminæ. In order to extract it, the gun-barrel is to be cut at the commencement of the part which has been kept cool, where the greatest quantity will be found. Another portion will be found close to the plug, and this adheres so slightly to the gun-barrel, that the least effort serves to detach it. It is even partly oxidized by the air, which gains access during the cooling of the furnace; and when the whole is covered with naphtha, the oxidized part is detached in laminæ, exposing a white and brilliant metallic surface.

The potassium, which is condensed nearest the furnace, must be detached by a sharp chisel, and in the largest pieces we can possibly break off; for if it be in small molecules, it inflames the air, even at very low temperatures. In the middle of the gun-barrel we shall find an amalgam of potassium and iron, which becomes green on exposure to the air, the potassium returning to the state of potash.

When the iron turnings were very clean, the potash very dry and pure, and the whole apparatus free from foreign matters, the metal produced differed very little from that obtained by a Voltaic battery. Its lustre, ductility, and malleability were similar. Its point of fusion and specific gravity, however, were a little higher; for it required nearly 130° Fahrenheit, to render it perfectly fluid, and was to water as 796 to 1000 at 60° Fahrenheit. This Sir H. Davy ascribes to contamination with a minute proportion of iron. The affinities, indeed, by which the decomposition is produced, he supposes to be those of iron for oxygen, of iron for potassium, and of potassium for hydrogen.

Charcoal, it has been asserted by Curaudu\*, may be employed, also, for the decomposition of the alkalies. To ensure success in the process, great attention, it appears, is necessary to the manipulations, which are fully described in the memoir of the inventor. The fact sufficiently explains an observation of Professor Woodhouset. A mixture of half a pound of soot and two ounces of pearlash, was exposed for two hours in a covered crucible to an intense heat. When the mixture became cold it was emptied upon a plate, and a small quantity of water poured upon it, when it immediately took fire. This could only be owing to the conversion of part of the potash into potassium.

### ART. 3.—Potassium.

I. The base of potash, at 60° Fahrenheit, exists in small globules, which possess the metallic lustre, opacity, and general appearance of

<sup>\*</sup> Nicholson's Journal, xxiv. 37. Vol. I.—A a

mercury; so that when a globule of mercury is placed near one of potassium, the eye can discover no difference between them. At this temperature, however, the metal is only imperfectly fluid; at 70° it becomes more fluid; and at 150° its fluidity is so perfect, that

several globules may easily be made to run into one.

By reducing its temperature, potassium becomes, at 50° Fahrenheit, a soft and malleable solid, which has the lustre of polished silver. At about the freezing point of water, it becomes hard and brittle, and exhibits, when broken, a crystallized texture, which, in the microscope, seems composed of beautiful facets of a perfect whiteness and high metallic splendor.

To be converted into vapour, it requires a temperature approaching that of a red heat; and when the experiment is conducted under

proper circumstances, it is found unaltered after distillation.

II. Potassium is a perfect conductor both of electricity and of heat.

III. Its specific gravity at  $60^{\circ}$  Fahrenheit, making some allowance for unavoidable errors in the experiment, is as 6 to 10, the latter number being assumed as that of water. Gay Lussac and Thenard make it between 8 and 9, and Bucholz 8.76; but they probably operated on a less pure substance. Even in its solid form, it swims in naphtha, whose specific gravity is about  $7\frac{1}{2}$  to 10. The most recent statement of its specific gravity, by Sir H. Davy, fixes it between 8 and 9.

IV. Its combustibility has already been noted. At the temperature of the atmosphere, it absorbs oxygen slowly; but if heated nearly to redness, or to its point of vaporization, it burns with a

brilliant white flame and a very intense heat.

V. It appears to be susceptible of different degrees or stages of oxidizement. 1stly, By heating it to a point, below what is necessary for its inflammation, either in common air or oxygen gas; or, (which is still better) by confining it, for some days, in an empty phial loosely corked, a substance is formed of a bluish grey colour, softer than wax, and readily fusible. This substance takes fire in oxygen gas, or even common air, at about 70° Fahrenheit, and acts on water, giving out hydrogen, but in less quantity than is extricated by potassium.

2. The second oxide is potash, which is most effectually produced

by the action of potassium on water.

3. Potassium, gently heated on a platinum tray in oxygen gas, gives, for the result of its combustion, an orange coloured fusible substance. It is necessary to protect the platinum from its action, by dipping the tray, before the experiment, into muriate of potash melted by heat. The precise nature of this compound was first explained, and its properties examined, by Gay Lussac and Thenard. It is fusible at a lower heat than hydrate of potash, and crystallizes in laminæ by cooling. When thrown into water, oxygen gas is evolved, and the substance passes, by this loss of oxygen, to the state of potash. Oxygen gas is, also, separated, by heating it strongly on a platinum tray coated with muriate of potash; and a grey vitreous

substance remains, which Sir H. Davy considers as absolutely pure potash. Almost all bodies, that have an attraction for oxygen, decompose this orange oxide, and reduce it to the state of potash, which in some cases, combines with the new compound. Charcoal, for example, with the excess of oxygen in the orange substance, forms carbonic acid; and this acid, uniting with the potash that is produced,

composes carbonate of potash.

VI. The action of potassium on water is attended with some beautiful phenomena. When it is thrown upon water exposed to the atmosphere, or when it is brought into contact with a drop of water, it decomposes the water with great violence; an instantaneous explosion is produced with a vehement flame; and a solution of pure potash is the result. The hydrogen gas, which is disengaged, appears to dissolve a portion of potassium; for, on escaping into the air, it forms a white ring of smoke, gradually enlarging as it ascends, like the phosphureted hydrogen gas.

When water is made to act on the base of potash, atmospheric air being excluded, there is much heat and noise, but no luminous appearance; and the gas evolved is pure hydrogen. It is of importance to remember that each grain of potassium, by acting on water,

detaches about 1.06 cubic inch of hydrogen gas.

If a globule of the base of potash be placed on ice, it instantly burns with a bright flame, and a deep hole is made in the, ice filled

with a fluid which is found to be a solution of potash.

The production of alkali, by the action of water on potassium, is most satisfactorily shown, by dropping a globule of the metal upon moistened paper, which has been tinged with turmeric. At the moment when the globule comes into contact with the paper, it burns, and moves rapidly as if in search of moisture, leaving behind it a deep reddish brown trace, and acting upon the paper exactly like dry caustic potash.

So strong indeed is the affinity of potassium for oxygen, that it discovers and decomposes the small quantities of water contained in alcohol and ether, even when carefully purified, and disengages,

from both these fluids, hydrogen gas.

On naphtha colourless and recently distilled, potassium has very little power of action; but in naphtha, which has been exposed to the air, it soon oxidates, and alkali is formed, which unites with the

naphtha into a brown soap, that collects round the globules.

VII. When thrown into the liquid mineral acid, the base of potash inflames, and burns on the surface; or, if kept beneath the surface, its effects are such as may be explained by its affinity for oxygen. In concentrated sulphuric acid, a white saline substance is formed, which is probably concentrated sulphuric acid surrounded by sulphur. At the same time a gas escapes which has the smell of sulphurous acid mixed with hydrogen gas. In nitrous acid, nitrous gas is disengaged, and nitre of potash is formed. In oxymuriatic acid gas, it burns vividly with bright scintillations, and muriate of potash is generated.

VIII. Potassium readily combines with the simple combustibles.

To unite it with sulphur or phosphorus, it must be melted with these bodies under naphtha.

The phosphuret of potassium requires for its fusion a stronger heat than either of its constituents. It is of the colour of lead; and, when spread out, has a lustre similar to polished lead. By exposure to the air, or by rapid combustion, forms phosphate of potash. Besides this, there is, also, a chocolate coloured compound of potassium and phosphorus; so that it is probable these two bodies unite in different proportions, the lead coloured compound consisting of 2 atoms of metal + 1 of phosphorus; and the chocolate of 1 atom of metal + 1 of phosphorus.

When potassium is fused with sulphur, in a vessel filled with the vapour of naphtha, a rapid combination ensues, accompanied with heat and light, and a disengagement of sulphureted hydrogen. The result is a grey substance not unlike artificial sulphuret of iron. Its formation and properties have been investigated by Vauquelin\*.

IX. With mercury, potassium gives some extraordinary and beautiful results. The combination is very rapid, and is effected by merely bringing them into contact at the temperature of the atmosphere. The amalgam, in which the potassium is in least proportion, seems to consist of about 1 part in weight of basis and 70 of mercury. It is very soft and malleable; but by increasing the proportion of potassium, we augment, in a proportional degree, the solidity and brit-

tleness of the compound.

The compound of mercury and potassium may be obtained by an easy and simple process, first pointed out by Berzelius. Mercury, to the depth of a line, is put into a glass capsule, two inches in diameter, with a flat bottom. On this a solution of pure potash is poured; an iron wire connects the mercury with the negative pole of a galvanic arrangement, which needs not contain more than 20 pairs of plates; and a spiral platina wire, from the positive pole, is immersed in the solution, and kept within about a line from the surface of the mercury. In six hours, the effect is observable, and in 24 is very distinct: for in that time, more than 1200 grains of mercury will be rendered solid by combination with potassium. Unfortunately, this combination cannot be so decomposed, as to obtain the potassium in a separate state.

In this state of division, potassium appears to have its affinity for oxygen considerably increased. By a few minutes exposure to the air, potash is formed which deliquiates, and the mercury is left pure and unaltered. When a globule is thrown into water, it produces a rapid decomposition and a hissing noise; potash is formed; pure

hydrogen disengaged; and the mercury remains free.

The fluid amalgam of potassium and mercury dissolves all the metals; and in this state of union, mercury even requires the power of acting on platina.

Potassium unites, also, with gold, silver, and copper; and, when the compounds are thrown into water, this fluid is decomposed,

<sup>\*</sup> Ann de Chim. et. Phys. vi. 22.

potash is formed, and the metals are separated unaltered. When the reduction of an ore has been accomplished by the use of fluxes containing potash, M. Vauquelin has shown that the revived metal contains a greater or less proportion of potash, which modifies its properties. By exposure to the air, or by the action of water, this

impurity may be removed\*.

X. Potassium, reduces all the metallic oxides when heated with them, even of those metals which most powerfully attract oxygen, such as oxides of iron. In consequence of this property it decomposes and corrodes flint and green glass by a very gentle heat; potash is generated with the oxygen taken from the metal, which dissolves the glass and exposes a new surface. At a red heat even the purest glass, formed merely of potash and silex, is acted upon. The alkali in the glass seems to give up a part of its oxygen to the potassium, and an oxide of potassium results, with a less proportion of oxygen than is necessary to constitute potash. The silex, also, it is probable, is partly de-oxidized.

From this summary of the action of potassium, it appears that all the most remarkable effects which it exhibits, are connected with its affinity for oxygen, which is sufficiently energetic to enable it to take oxygen from all other bodies. Hence the application of potassium to any substance is the best test of its containing oxygen, which,

if present, it cannot fail to detect.

It was important to determine the proportions in which potassium and oxygen combine, when potash is regenerated. This Sir H. Davy investigated by two different processes. The one consisted in ascertaining how much oxygen gas disappears by the action of a given quantity of potassium; the other how much hydrogen is disengaged from water by a known weight of the same substance. Dividing the bulk of the hydrogen gas by 2, he learned the quantity of oxygen which had been taken from the water.

The coincidence of results, obtained by these different methods, is remarkable. By the action of potassium on oxygen gas, it ap-

peared, on an average, that

Potash consists of \{ 86.1 potassium, 13.9 oxygen.

100.

By the agency of water, the proportions differed only by a small fraction, so that we may state in round numbers that the base is to the oxygen as six to one, or that

Potash is composed of \{ 86 potassium, 14 oxygen.

100.

Subsequent experiments, however, have made some change necessary in these numbers. Gay Lussac and Thenard found, that 100 parts by weight of potassium take 19.945 of oxygen from water; and

<sup>\*</sup> Ann. de Chim. et Phys. vii. 32.

Sir H. Davy, by the action of 8 grains of potassium on water, obtained, on an average, .9½ cubic inches of hydrogen gas, showing that 4¾ cubic inches, (= 1.61 grains) of oxygen had combined with the metal. Berzelius investigated the composition of potash, by exposing an amalgam of potassium and mercury, containing known proportions of those metals, to water; saturating the potash with muriatic acid; and determining its weight by the muriate potash formed\*. The following table shows the proportions of potassium and oxygen in 100 grains of potash, as deduced from these different authorities. One hundred grains of potash contain,

					Pot	assium.	Oxygen.
According to Sir H. Davy	•			•		83.2	16.8
According to Sir H. Davy Gay Lussac						13.37	16.63
Berzelius .	•	•			•	82.97	17.03

If deducted from the atomic theory, the true proportions should be 85 of potassium to 15 oxygen, numbers very near those originally obtained by Sir H. Davy. It is probable, indeed, that sources of inaccuracy may exist in the experiments, sufficient to account for this small deviation from theory; and that potash is a compound of 1 atom of potassium weighing 42.5 with 1 atom of oxygen weighing 7.5. Hence the weight of the atom of potash will be 50; and an atom of water (8.5) being added, the atom of hydrate of potash will weigh 58.5.

It is doubtful whether the grey compound (mentioned in § v). be a true sub-oxide of potassium, or merely a mixture of potash with potassium. If the former, it must consist of two atoms of potassium (85) with one atom of oxyged (7.5—92.5. But the latter view of its

nature is the most probable one.

The composition of the orange oxide cannot be assigned, from the quantity of oxygen, absorbed in the experiments, by which it is produced; for in eight results, obtained by Gay Lussac and Thenard, there is not a sufficient agreement to decide this point. It seems probable that the oxygen, which converts potassium into this substance, is twice that which converts it into potash; and that the orange oxide consists of 1 atom of potassium = 42.5, + 2 atoms of oxygen = 15, which would make the weight of the atom of orange oxide 57.5.

# Potassureted Hydrogén Gas.

This name I would propose for the solution of potassium in hydrogen gas, which, it has already been stated, results from the action of potassium on water, and, and as appears from Sir H. Davy's experiments, may be formed, directly, by heating the metal in hydrogen gas. A large portion of potassium is thus dissolved; but the greater part precipitates on cooling.

This gas is spontaneously inflammable in the atmosphere; burns

<sup>\* 80</sup> Ann. de Chim. 245.

with a very brilliant light, which is purple at the edges; and throws off dense vapours of potash. It loses its inflammability by keeping; is heavier than hydrogen gas; and is very dilatable by electricity. Besides the gas, which is spontaneously combustible, there is also, according to Sementini, another compound of potassium and hydrogen, which is not possessed of this property, and probably contains a less proportion of the combustible metal.

Gay Lussac and Thenard\* have succeeded, also, in forming a solid compound of potassium and hydrogen. The process consists in heating the metal in hydrogen gas; and the only difficulty is to regulate the heat, for a temperature decomposes the compound. The flame of a spirit lamp, applied to potassium, in a retort filled with hydrogen gas, occasions an absorption of the gas, and the formation

of a solid hydruret of potassium.

The colour of the substance is grey; it is destitute of metallic lustre; and is infusible. It is not inflammable, either in air or in oxygen gas at common temperatures, but burns vividly at a high one. When strongly heated in a close vessel, it is totally decomposed; all the hydrogen it contains is liberated in the state of gas; and the potassium remains. When brought into contact with heated mercury, hydrogen gas is evolved, and an amalgam of potassium and mercury is produced.

Nitrogen gas has not, at any temperature, any action on potas-

sium.

### ART. 4.—Sodium.

The base of soda agrees, in many of its properties, with the base of potash, and exerts on several bodies a similar action, with the obvious exception that the results are compounds of soda instead of potash. Thus with nitric acid it affords nitrate of soda; with oxy-muriatic acid, muriate of soda. In this place, therefore, I shall describe only such of its properties as are peculiar to and characteristic of it.

I. Sodium, at common temperatures, exists in a solid form. It is white, opaque; and, when examined under a thin film of naphtha, has the lustre and general appearance of silver. It is exceedingly malleable, and much softer than any of the common metallic substances. When pressed upon by a platinum blade with a small force, it spreads into thin leaves; and a globule of the orange of an inch in diameter is easily spread over the surface of a quarter of an inch. This property is not diminished by cooling it to 32° Fahrenheit. Several globules, also, may, by strong pressure, be forced into one; so that the property of welding, which belongs to platinum and iron at a high degree of heat only, is possessed by this substance at common temperatures.

II. It is lighter than water. As near as can be determined, its

specific gravity is as 0.9348 to 1.

Recherches, i. 176.

III. It is much less fusible than the base of potash. At 120° Fahrenheit, it begins to lose its cohesion, and it is a perfect fluid at about 180°. Hence it readily fuses under heated naphtha.

IV. Its point of vaporization has not been ascertained; but it remains fixed, in a state of ignition, at the point of fusion of plate

glass.

V. When SODIUM is exposed to the atmosphere, it immediately tarnishes, and by degrees becomes covered with a white crust of soda, which deliquiates more slowly than that formed on potassium.

VI. It combines with oxygen, slowly and without luminous appearance, at all common temperatures. When heated, the combination becomes more rapid; but no light is emitted till it becomes nearly red hot. The flame, which it then produces, is white, and it sends forth bright sparks, exhibiting a very beautiful effect. In common air, it burns with a similar colour to charcoal, but of much greater splendour.

VII. When thrown into water, it produces a violent effervescense and a loud hissing noise; it combines with the oxygen of the water to form soda; and hydrogen gas is evolved, which does not, however, as in the case of potassium, hold any of the alkaline base in solution. Neither can sodium be made to dissolve in hydrogen gas, by being

heated in contact with it.

When thrown into hot water, the decomposition is more violent, and in this case a few scintillations are generally observed at the surface of the fluid; but this is owing to small particles of the base, which are ejected from the water, sufficiently heated to burn in passing through the atmosphere.

VIII. Its action on alcohol, ether, volatile oils, and acids, is similar to that of potassium; but with nitric acid a vivid inflammation is

produced.

IX. Sodium appears to be susceptible of different degrees of oxydation. 1st. When it is fused with dry soda, a partition of oxygen takes place between the alkali and the metal. A deep brown fluid is produced, which becomes a dark grey solid on cooling. This substance is capable of attracting oxygen from the atmosphere, and of decomposing water, by which it is again converted into soda. The same oxide of sodium is formed, by fusing this metal in tubes of plate glass.

It is of a greyish colour, destitute of lustre, brittle, and gives hydrogen when acted on by water, but less than an equal weight of sodium. It may, however, be doubted, whether this is a compound of sodium and oxygen, or merely a mixture of the metal with soda.

2d. The second oxide of sodium (or first, if the one which has been just described be only a mechanical mixture) is soda. It may be formed by burning sodium, in a quantity of air containing just oxygen enough to convert the metal into alkali. It is of a grey colour; of a vitreous fracture; and requires a strong red heat for its fusion. Water is absorbed by it with violence, and converts it into hydrate of soda.

3d. The orange oxide of sodium may be formed, by burning the

metal with an excess of oxygen. It is of a deep orange colour, very fusible, and a non-conductor of electricity. When acted on by water, its excess of oxygen escapes, and it becomes soda. It defla-

grates with most combustible bodies.

X. There is scarcely any difference between the visible phenomena attending the action of the base of soda, and that of potash on sulphur, phosphorus and the metals. The sulphuret of sodium has a deep grey colour; the phosphuret resembles lead. Added to mercury in the proportion of  $\frac{1}{40}$ th, it renders that metal a fixed solid of the colour of silver, and the combination is attended with a considerable degree of heat. This amalgam seems, like that of potassium, to form triple compounds with other metals, and even with iron and platinum, which remain united with the mercury, when it is deprived of the new metal by the action of air.

The proportions, in which this base unites with oxygen to form soda, were investigated by the methods already described in the article Potassium. The results of Sir H. Davy; of Gay Lussac and The-

nard; and of Berzelius, are given in the following table:

												socium.	Uxygei
Per Davy (1807)	100	sod	a	cor	ta	in	•	•		•	•	77.7	22.3
Per Davy (1807)  — Ditto (1811)  — Gay Lussac							•	•,	•	•	•	<b>74.6</b>	25.4
- Gay Lussac			,	•		•		•	•	•		<b>74.63</b>	25.37
- Berzelius *.	•	• ,		•	•	•	•	•	•	•	•	74.29	27.71

The proportions that would best accord with the atomic theory, are 77.5 of sodium to 22.5 of oxygen; for this last number agrees with the weight of three atoms of oxygen. And on the supposition that soda is a compound of 1 atom of sodium  $\times$  1 atom of oxygen, by dividing 77.5 by 3 we should obtain the weight of the atom of sodium, viz. 25.8. In this case, the atom of soda would weigh 33.3, and the atom of hydrate of soda 41.8. The number assumed by Dr. Wollaston to represent sodium, (oxygen being 10) is 29.1; and soda will, therefore, be denoted, on his scale, by  $29.1 \times 10 = 39.1$ . The peroxide Dr. Thomson is disposed to consider as a compound of two atoms of sodium with three atoms of oxygen.

## SECTION II.

### Lithia or Lithina.

THE discovery of this new substance, which dates only from the commencement of the present year, is due to the skill and sagacity of M. Arfvredson, a pupil of Berzelius. In the analysis of a mineral called *Petalite*, (first distinguished as a new species by M. D'Andrada, who found it in the mine of Uto, in Sweden), about 3 per cent. of an alkali was obtained, which M. Arfvredson at first supposed to

<sup>• 80</sup> Ann. de Chim. 251.

<sup>†</sup> Ann. of Phil. x. 100.

be soda. On more accurate examination, however, the new substance displayed properties, entirely distinct from those of either soda or potash, especially in possessing the power of neutralizing a much greater quantity of the different acids than either of those alkalies; in which respect it even surpassed magnesia. To distinguish it from the two other fixed alkalies, both of vegetable origin, it received the name of lithion; and this term, to suit the analogy of the other al-

kalies, was afterwards converted into lithia or lithina.

The proportion of lithina in petalite has since been found to be 5 per cent.; and from some very pure pieces of that mineral, Vauquelin has extracted even 7 per cent. M. Arfvredson has discovered it, to the amount of 8 per cent. in triphane or spodumene, a mineral which is not so scarce as petalite; and, to the extent of 4 per cent. in crystallized lepidolite. The process employed by him has not been described; but it probably consisted in fusing the mineral with twice or three times its weight of potash; dissolving the fused mass in muriatic acid; evaporating to dryness; and digesting in alcohol, which takes up scarcely any thing but a compound of the new earth with muriatic acid. By evaporating a second time to dryness, and again dissolving in alcohol, the muriate of lithina is obtained pure. Vauquelin extracted it from petalite by the intervention of nitrate of barytes, employed, probably, in the manner which will be described in the chapter on the analysis of minerals.

The muriate of lithina may be decomposed by digestion with carbonate of silver; and the solution of the carbonate, being decomposed by lime or by barytes, yields a solution of pure lithina, which may be evaporated to dryness out of contact with the air, from which it

rapidly imbibes carbonic acid.

Pure lithina is very soluble in water, and, like the other alkalies, has an acrid, caustic taste. Like them also, it changes vegetable blue colours to green. When heated in contact with platinum, it fuses, and then acts on the metal. That it agrees with the other alkalies in containing a metallic base, has been proved by Sir H. Davy, who applied the power of a galvanic battery to a portion of the carbonate, fused in a platinum capsule. On rendering the platinum positive, and bringing a negative wire to the surface of the fused carbonate, the alkali was decomposed with bright scintillations; but the reduced metal burned again so rapidly, that it was only observed to be of a white colour and very similar to sodium. From analogy, it has received the name of lithium. The proportion, in which this metal unites with oxygen, has, of course, not been determined by direct experiment; but it has been deduced by Vauquelin, from an analysis of the sulphate of lithina, and the application of the law that the proportion between the oxygen of sulphuric acid, and that of the bases which it saturates, is as 3 to 1", to be as follows:

Lithium				56.50	•.			100		• ` •	 . :	130
Oxygen				43.50				77				100

It would be premature, in the present imperfect state of our knowledge of this new metal and alkali, to determine their equivalents, or in other words, the weights of their atoms.

Instead, also, of describing the compounds of lithina, like those of the other alkalies, in future parts of the work, I shall state, in this

place, the little that is known respecting them.

With sulphur, lithina affords a yellow, and very soluble compound, which is decomposed by acids, with the same phenomena as the alkaline sulphurets, and, from the abundance of the precipitate, appears to contain a large proportion of sulphur.

Sulphate of lithina crystallizes in small prisms of a shining white colour. It is more fusible and soluble than sulphate of potash, and has a saline, not a bitter taste. It is constituted of

Sulphuric acid . . . . . . 69.20 Lithina . . . . . . . . . . . . 31.80

100.

The muriate and the nitrate of lithina are both deliquescent salts. The carbonate is efflorescent in the air, and is sparingly soluble, requiring about 100 times its weight of cold water. The solution effervesces with acids; changes vegetable blue colours to green; decomposes solutions of alumine and magnesia, and of the metals; disengages ammoniac from its combinations; and does not precipitate the muriate of platinum. The dry carbonate, when fused on platinum, acts as powerfully on that metal as the alkaline nitrates. The tartrate of lithina is an efflorescent salt; and the acetate, when evaporated, assumes the consistence of gum or syrup\*.

#### SECTION III.

### Pure Ammonia.

# ART. 1.—Preparation and Qualities of Ammonia.

I. Ammonia, in its purest form, exists in the state of a gas. In order to procure it, one of the following processes may be employed.

(a) Mix together equal parts of muriate of ammonia and dry quicklime, each separately powdered; and introduce them into a small gas bottle or retort. Apply the heat of a lamp; and receive the gas, that is liberated, over mercury.

(b) To a saturated solution of ammonia in water or the pure liquid ammonia, in a gas bottle, apply the heat of a lamp; and collect

the gas, as in a.

II. This gas has the following properties:

(a) It has a strong and very pungent smell.
(b) It immediately extinguishes flame; and is fatal to animals.
Before, however, a candle is extinguished, by immersion in this gas,

<sup>\*</sup> See Thomson's Annals, xi. 291, 373, 447; xii. 15; Ann. de Chim. et Phys. vii. 284, 313; and Journal of Science, &c. v. 337.

the flame is enlarged, by the addition of another, of a pale yellow colour, which descends from the mouth to the bottom of the jar. If the flame of the candle be only in part immersed in the gas, this

yellowish flame rises a few lines above the other.

(c) It is lighter than atmospheric air. Hence a jar filled with this gas, and placed with its mouth upwards, is soon found to exchange its contents for common air, which, being heavier, descends, and displaces the ammoniacal gas. By the recent experiments of Messys. Allen and Pepys\*, undertaken at the desire of Sir H. Davy, 100 cubic inches of ammonia weigh 18.18 grains, barometer 30, thermometer 60°. According to Gay Lussac, its specific gravity is to that of common air as 0.5967 to 10; and hence (taking 100 cubic inches of air at 30.5 grains) 100 cubic inches of ammonia weigh 18.17 grains. Mr. Dalton assumes, that at a mean temperature and pressure, 100 cubic inches weigh 18.6 grains; and hence that its specific gravity is 6, air being 10. It does not appear that in any of these trials, the gas was artificially dried. To effect its desiccation, potash or quicklime are best adapted; for dry muriate of cloride of lime, as well as several other chlorides, absorb it rapidlyt.

(d) Ammoniacal gas is not sufficiently inflammable to burn when in contact with common air. But, when expelled from the extremity of a pipe, having a small aperture surrounded by oxygen gas, it may be kindled, and it then burns with a pale yellow flame, the products

of its combustion being water and nitrogen gas.

(e) Ammoniacal gas may be decomposed by transmitting it through a red hot porcelain tube, which should be either well glazed internally, or covered externally with a lute. It has been ascertained by Thenardt, that when any of the five following metals are enclosed in the tube, they promote the decomposition of ammonia in the order set down, viz. iron, copper, silver, gold, and platinum: iron being most effectual, and platinum least. Iron, after the process, is found to be rendered brittle, and copper still more so. The gas obtained always consists of 3 parts hydrogen by measure, and 1 nitrogen. None of the metals is either increased or diminished in weight; and they can only, therefore, act as conductors of heat. Yet it is singular that iron decomposes a much larger quantity than platinum, and at a lower temperature.

(f) It has been asserted by Guyton, that ammoniacal gas is reduced to a liquid state at 70° below 0 of Fahrenheit; but it may be questioned whether the drops of liquid, which he observed, were any thing more than the watery vapour, which the gas always con-

tains, condensed by the cold, and saturated with ammonia.

(g) Ammonia is rapidly absorbed by water. A drop or two of water being admitted to a jar of this gas, confined over mercury, the gas will be immediately absorbed, and the mercury will rise, so as to fill the whole of the jar, provided the gas be sufficiently pure. Ice produces the same effect, in a still more remarkable manner.

<sup>\*</sup>Philosophical Transactions, 1818, page 39. † Journal of Science, v. 74. # 85 Ann. de Chim. 61.

From Sir H. Davy's experiments, it appears that 100 grains of water absorb 34 grains of ammoniacal gas, or 190 cubic inches. Therefore a cubic inch of water takes up 475 cubic inches of the gas. More recently he has stated that at 50° Fahrenheit, water absorbs 670 times its bulk, and acquires the specific gravity .875\*.

Alcohol, also, absorbs several times its bulk, and affords a solution of ammonia in alcohol, which possesses the strong smell, and other

properties, of the gas.

(h) Water, by saturation with this gas, acquires its peculiar smell; and constitutes what has been called liquid ammonia; or, more properly, solution of pure ammonia in water. The method of effecting this impregnation will be described hereafter; the processes will be given for obtaining the solution of ammonia in considerable quantity, which cannot conveniently be accomplished by the method described in experiment e. This solution again yields its gas on applying heat. (See I. b.)

The strength of a solution of ammonia is influenced by two circumstances, the temperature of the liquid, and the pressure on its surface, for ammonia is not retained in water without external force. The intervals of temperature, required to double the force of ammoniacal vapour, were ascertained by Mr. Dalton to increase in ascending. When mixed with common air, its elasticity is not altered; thus when ammoniacal gas of 15 inches force is mixed with a

given volume of air, the air is doubled in bulk.

Solutions of ammonia, when mixed with water, were found by Sir H. Davy, not to be sensibly condensed; and, therefore, if the quantity of ammonia in a solution of given specific gravity be determined, it is easy to calculate the quantity in solutions of other densities. The two following Tables, it may be observed, do not exactly agree in their results, the quantity of ammonia, in solutions of the same density, being from 15 to 20 per cent. less in Mr. Dalton's Table than in Sir H. Davy's. The numbers in the latter, marked with an asterisk, were found by experiment, and from these the others were deduced.

Sir H. Davy's Table of the Quantities of Ammoniacal Gas in Solutions of different Densities (Temp. 50° Fahrenheit's Barometer, 29.8).

100 parts of Specific Gravity.	Of Ammonia.	100 parts of Specific Gravity.		Of Ammonia.
.8750* .8875 .9000 .9054* .9166 .9255 .9326	32.5 29.25 26. 25.37 22.07 19.54 17.52 15.88	.9435 .9476 .9513 .9545 .9573 .9597 .9619 .9692*	contain	14.53 13.46 12.40 11.56 10.82 10.17 9.60 9.50

Elements of Chem. Phil. p. 263.

Mr. Dalton's Table of the Quantities of Ammonia in Solutions of different specific Gravities.

Specific Gravity.	Grains of Ammonia in 100 water-grain measures of liquid.	Grains of Am- monia in 100 grains of liquid.	of the liquid	Volumes of gas dondensed in a given volume of liquid.
850	50	35.3	26°	494
860	28	32.6	38°	456
870	26	29.9	50°	419
880	24	27.3	62°	382
890	22	24.7	74°	346
900	20	22.2	86°	311
910	18	19.8	- 5850	277
920	16	17.4	1100	244
930	14	15.1	129°	211
940	12	12.8	134°	180
950	10	10.5	146°	147
960	8	8.3	158°	N16
970	6	6.2	175°	87
980	4	4.1	187°	57
990	2	2.	196°	28

ART. 2.-Electrical Analysis of Ammonia.

(1) Ammoniacal gas is decomposed by electricity. Into a glass tube, having a conductor sealed hermetically into one end (fig. 29). and standing inverted over mercury, pass about one tenth of a cubid inch of ammoniacal gas; and transmit through it a succession of electrical discharges from a Leyden jar. The arrangement of the apparatus, for this purpose, is shown in fig. 84, pl. ix. and is described in chap. v. sect. 1. When two or three hundred discharges have been passed, the gas will be found to have increased to almost twice its original bulk, and to have lost its property of being absorbed by water. Mix it with a quantity of oxygen gas, equal to between one third and one half of its bulk, and pass an electric spark through the mixture. An explosion will immediately happen; and the quantity of gas will be considerably diminished. Note the amount of the diminution by firing; divide it by 3; and multiply the product The result shows the quantity of hydrogen gas in the mixed gases which have been generated by electricity; for two measures of hydrogen are saturated by one of oxygen gas.

Suppose, for example that we expand 10 measures of ammonia to 18; and that, after adding 8 measures of oxygen gas, we find the whole (=26 measures) reduced by firing to 6 measures; the diminution will be 20. Dividing 20 by 3 we have 6.66, which multiplied by 2 gives 13.32 measures of hydrogen gas from 10 of ammonia. Deducting 13.32 from 18, we have 4.68 for the nitrogen gas contained in the product of electrization. Therefore 10 measures of ammonianed in the product of electrization.

nia have been destroyed, and expanded into

## 13.32 measures of hydrogen gas, 4.68 ——nitrogen gas.

According to the above proportions, 100 cubic inches of ammonia, which weigh about 18 grains, if they could be decomposed by electricity, would give about 133 cubic inches of hydrogen, weighing \$.5 grains, and 46 of nitrogen weighing 14.4 grains, in all 17.9 grains, or one tenth of a grain less than the ammonia decomposed. Mr. Dalton obtained 185 measures of gas by decomposing 100 measures of ammonia; and, by comparing the products with the original gas, he finds that the weight of the former rather exceeds that of the latter thus,

100 measures of ammonia  $\times$  sp. gr. .6 = 60produce  $\begin{cases} 51.8 \text{ nitrogen, which } \times \text{ sp. gr. } .967 = 50.09 \\ 183.2 \text{ hydrogen, which } \times \text{ sp. gr. } .08 = 10.65 \\ \hline 60.74 \end{cases}$ 

The excess of 3ths of a grain in 60 he considers as too small to affect the conclusion, and as arising from unavoidable inaccuracies in some of the data.

It is contended by Gay Lussac and Thenard, and the probable accuracy of their result is admitted by Sir H. Davy\* and by Dr. Wollaston, that 200 measures of ammonia are resolvable, by analysis, into 300 of hydrogen and 100 of nitrogen. This proportion is consistent with the theory of combination in definite volumes. There is, however, considerable difficulty in ascertaining the precise amount of the gases evolved from ammonia; for if either the gas itself, or the mercury which confines it, contain any moisture, the product of gas, resulting from its decomposition, will exceed what it ought to be. The problem is one of great importance to the atomic theory, because from the proportion of the elements of ammonia, is deduced the weight of the atom of nitrogen. This will differ considerably, according to the statement, which we may adopt, of the amount of gases obtained by decomposing ammonia; their proportion to each other; and the exact specific gravities of hydrogen and nitrogen gases. From the data supplied by Mr. Dalton, it appears reasonable to believe, that the weight of nitrogen in ammonia is to that of hydrogen nearly as 5 to 1, and the atom of nitrogen will, therefore, be represented by 5, and that of ammonia by 5 + 1 = 6. (In the scale of Dr. Wollaston, nitrogen is represented by 17.54; which, with 3 proportions of hydrogen  $(1.32 \times 3 = 3.96)$ , gives 21.5 for the equivalent of ammonia.

(2) In the Philosophical Transactions for 1809, I have described a property of ammonia, which forms the basis of a very easy and quick mode of analyzing that alkali. When mingled with oxygen

<sup>\*</sup> Elements of Chem. Phil. p. 269.

gas it may be inflamed by the electric spark, precisely like a mixture of hydrogen and oxygen gases. To obtain accurate results, however, it is necessary to use less oxygen at first, than is sufficient to saturate the whole hydrogen of the alkali. This is easily calculated. If, for example, we take 10 measures of ammonia, we must use less oxygen than will saturate 13 or 14 measures of hydrogen gas, the quantity which exists in 10 of ammonia; and which require about 7 of oxygen gas. It will be adviseable, therefore, not to add above 4 or 5 of oxygen. The whole (suppose 15) will probably, after firing, be reduced to about 9. To the remaining gas admit 4 or 5 measures more of oxygen; and on passing the electric spark again, a second explosion will happen, with a diminution of about 6 measures. But, in the first explosion, the whole of the oxygen disappears, and it must therefore have saturated a quantity of hydrogen equal to 10 measures; besides which, two thirds of the second diminution  $(6 \div 3 \times 2)$ = 4 measures are owing to the condensation of hydrogen. the whole hydrogen is 10 + 4 = 14. The nitrogen, the whole of which exists in the product of the first detonation, is ascertained by deducting from it (viz. from 9 in the present instance) the second quantity of hydrogen (4) which gives 5 for the nitrogen. These numbers may not, perhaps, be exactly obtained by experiment; and they are given merely as a general illustration of the process.

By experiments of this kind, I have determined that 100 measures of ammonia require, for saturating the hydrogen which they contain,

between 67 and 68 of pure oxygen gas, and afford

Of hydrogen gas about 136 measures, nitrogen gas . . . . 47 measures.

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The results of this analysis furnish a good example of the condensation of the elements of gases which takes place on chemical union; and if we could, by any means, permanently condense a mixture of 136 measures of hydrogen with 47 of nitrogen into 100 measures, the new gas would constitute ammonia. Simple admixture of these gases, however, even in the same proportions which are obtained by analyzing ammonia, is not sufficient to generate this alkali. The caloric, with which the hydrogen and nitrogen are respectively combined, opposes, by its elasticity, an obstacle to their union, and places them beyond the sphere of their mutual attractions. If these elements are presented to each other when one or both are deprived of part of their caloric, combination then takes place; and the composition of the volatile alkali is proved synthetically, as in the following experiment.

When iron filings, moistened with water, are exposed to nitrogen gas confined over mercury, the gas, after some time has elapsed, acquires the smell of volatile alkali. In this case, the iron decomposes the water and seizes its oxygen; while the hydrogen, at the moment of its liberation, unites with nitrogen and composes ammonia. This state of condensation, or absence of the quantity of caloric necessary to bring it into a gaseous form, has been called the nascent state of

hydrogen; and the same term has been applied to the bases of other gases when in a similar state.

## ART. 3.—On the Presence of Oxygen in Ammonia; and on the Amalgam of Mercury and Ammonia.

Beside the hydrogen and nitrogen which, it has already been stated, are obtained by decomposing ammonia, it has been conjectured by Sir H. Davy that this alkali contains, also, a small proportion of oxygen, not exceeding seven or eight parts in the hundred. The arguments, which he has brought in favour of this opinion, are derived chiefly from the following facts:

1. When he decomposed ammonia by electricity, the gases produced fell short, by nearly one eleventh, of the weight of the ammonia employed; in other words, 100 grains of ammonia gave only about 91 grains of permanent gases. To obtain this result, however, several precautions are necessary, which are fully stated in the Phi-

losophical Transactions for 1809, p. 460.

2. By repeatedly transmitting ammoniacal gas (previously deprived, by passing it through a tube surrounded by a freezing mixture, of as much water as possible (over red-hot iron wire, the metal became superficially oxidized, and gained a very slight increase of weight. It is proper, however, to state, that a similar experiment was made by M. Berthollet, junior, with different, or at least with equivocal, results. Besides, a very minute addition of oxygen might be furnished to the iron by the decomposition of a small por-, tion of water, which ammoniacal gas, in common with all other gases, contains; and which would scarcely be separated from it by the temperature of a freezing mixture. No sufficient proof, indeed, has been established by the subsequent experiments of Sir H. Davy; by my own, directed to the same object; or by those of any other person, that oxygen exists as an element of ammonia, or that any products can be obtained by its decomposition, beside hydrogen and nitrogen gases.

It must be acknowledged, however, that the indirect evidence, in favour of the presence of oxygen as an element of ammonia, which is furnished by other experiments of Sir H. Davy, is much stronger than that derived from the results of its analysis. These experiments even go so far as to suggest that ammonia may, like the fixed alkalies, be an oxide of a peculiar metal, or at least of some compound containing the elements of a metal. And, as hydrogen and nitrogen alone are obtained by the electrical analysis of ammonia, it will follow that the metal in question is either a compound of those two bases, or a component part of one of them. If this should be established, we shall obtain proof of a fact of the greatest novelty and curiosity, viz. the existence of a metal or a metallic oxide,

whose natural state is that of an aëriform fluid.

To understand the general outline in these experiments, it may Vol. I.—Cc

be necessary to premise, that whenever mercury, after combination with another substance, retains in a great measure its characteristic properties, and forms what has been called an amalgam, we infer that the change has been produced by its union with a metal; for the metals are the only bodies which are capable of amalgamating with quicksilver. Now it was found, by MM. Berzelius and Pontin of Stockholm, that when mercury, negatively electrified in the Voltaic circuit, is placed in contact with solution of ammonia, it gradually expands to four or five times its dimensions, and becomes a soft solid, which, at 70° or 80° Fahrenheit, has the consistence of butter. the freezing temperature, it becomes firmer, and forms a crystallized mass, in which small shining facets appear. By this combination, it is very remarkable that mercury gains an addition of only about one twelve thousandth part of its weight; and yet has its specific gravity so much decreased, that from being between 13 and 14 times heavier than water, it becomes only three times heavier. Its colour, lustre, opacity, and conducting powers remain unimpaired.

An easier mode of forming this amalgam, Sir H. Davy found, is to employ mercury united with a minute quantity of potassium, sodium, or barium. A compound of this sort, placed in contact with a solution of ammonia, enlarges to eight or ten times its bulk, and becomes a soft solid, which may be preserved a much longer time than the amalgam made by electrical powers, and which even changes

very slowly under water.

When this amalgam is exposed to the atmosphere, oxygen is absorbed; ammonia is produced; and the quicksilver is recovered in its metallic form. When thrown into water, ammonia is also regenerated, and quicksilver separated, hydrogen gas being at the same time evolved. It appears, then, that in the formation of the amalgam, mercury combines with one or more of the elements of ammonia, and that in the subsequent oxidation of what is thus acquired by the ammonia, consists the process of regenerating alkali. In this view of the subject, there certainly appears great reason to believe that oxygen is one of the constituents of ammonia; but the facts are not sufficiently simple to furnish incontrovertible evidence, and their explanation is still attended with considerable obscurity.

On the supposition that the unknown substance, which amalgamates with the mercury, is of a metallic nature, Sir H. Davy proposed for it the name AMMONIUM. All attempts to detach it from this combination, and to exhibit it in a separate form, have hitherto failed; and it still remains an object of farther investigation. One great difficulty consists in procuring the amalgam free from water, of which it always contains enough to furnish oxygen, and to regenerate alkali. The amalgam, which appears to be most free from adhering moisture, is that of potassium, mercury, and ammonium in a solid state; but even this amalgam gave on distillation nothing but hydrogen gas, besides a small proportion of ammonia. The quantity of matter, added to the mercury, in the formation of the amalgam, Sir H. Davy estimates at only 12 550 th.

Gay Lussac an Thenard\* have also made a great number of experiments on this amalgam, from which they infer that it is a compound of mercury, hydrogen, and ammonia; and that mercury, to become the amalgam, absorbs 3.47 times its bulk of hydrogen gas, 4.22 or 3.67 times its bulk of ammoniacal gas. The increased levity of the mercury, they are of opinion, may be explained by the lightness of the elements with which it combines, and by their being retained by so feeble an affinity, as to produce very little condensation. This view of the subject has been opposed by Berzelius on theoretical grounds, for a statement of which the reader may consult the 77th vol. of Annales de Chimie, p. 79. In the present state of the inquiry, new facts seem to be wanting to determine the nature of this singular compound.

An experiment of Dobereiner would, if confirmed, prove that hydrogen has of itself the property of forming an amalgam with mercury. He introduced a globule of mercury into a vessel of water, and placed it near the negative wire of a galvanic battery. Oxygen gas was given out from the positive wire, but no gas whatever arose from the negative wire. By this wire, the mercury was attracted and gradually converted into an amalgamt. The experiment, however, when carefully repeated in this country, has not been attended

with the same result.

## ART. 4.—Action of Potassium on Ammonia.

When potassium is melted in ammoniacal gas, it is changed into an olive-green fusible substance; the ammonia almost entirely disappears; and is replaced by a volume of hydrogen, precisely equal to that, which the same quantity of potassium would have disengaged from water. To effect this combination, in the way recommended by Gay Lussac and Thenard, a bent glass tube is employed, into which, when filled with perfectly dry mercury, a known quantity of ammoniacal gas is admitted, and a determinate weight of potassium is then passed through the mercury, by means of a bent iron wire. Care must be taken to shake off from the potassium, and from that part of the tube which contains the gas, all the adhering globules of mercury; otherwise they interfere with the result. The part of the tube, which contains the potassium, is next gently heated by a spirit lamp; the metal enters into fusion, and is covered with a thin crust, which soon disappears; the brilliant surface of the metal then is exposed; it absorbs much ammoniacal gas, and, in a few instants, is transformed into the olive-green substance. It is necessary, at this period, to remove the lamp; and indeed the regulation of the heat, which can only be learned by experience, occasions considerable variety in the results, and in the quantity of ammonia which dis-When the gas is used in sufficient quantity, all the potassium is changed into the olive compound; and it absorbs from 100 to 136 times its volume of alkaline gas.

<sup>\*</sup> Recherches, i 72.

<sup>‡</sup> Phil. Mag. xlvi. 421.

<sup>†</sup> Thomson's Annals, vii. 30.

When the olive-coloured substance is gradually heated in a glass vessel, in contact with hydrogen gas, it enters into a kind of ebullition; much gas is disengaged; and the mercury descends rapidly in the tube. When the tube is not heated beyond a cherry red, nothing but ammonia is disengaged. But when this degree of heat is exceeded, hydrogen and nitrogen are obtained, in the proportions required to form ammonia, viz. 3 to 1. In all cases, the residue is blackish, and is found to have lost its fusibility. Only three fifths, however, of the ammonia which has disappeared, can be re-obtained by heat, either in the form of alkaline gas or of its elements.

When the olive-coloured substance is brought into contact with water in close vessels, great heat is excited, and the only products are potash and ammoniacal gas, the latter in exactly the same quantity which was originally absorbed, except a few hundredth parts, which are absorbed by the moist potash. The only caution, necessary to obtain this result, is not to use more water than is absolutely

necessary.

Precisely similar phenomena occur, when sodium is heated in ammoniacal gas; the sodium is transformed into an olive-green substance; ammonia is absorbed, and hydrogen is evolved, in exactly the same quantity as by the action of an equal weight of sodium on water.

The experiments of Sir H. Davy on the olive-coloured compound agree, in the main, with those of Gay Lussac and Thenard. By distillation per se, he obtained some undecomposed ammonia, and hydrogen and nitrogen gases in the proportion by volume of 2½ of the former to 1 of the latter. He examined the residue of its distillation with much attention; and describes it to be a black, shining, opaque, and brittle substance, highly inflammable when exposed to air at the ordinary temperature. When submitted by itself to distillation at a strong heat, in a platinum tube (which was done with the expectation that nitrogen gas only would have been evolved), a mixture of gases was obtained, consisting of only one fifth nitrogen, and four fifths hydrogen, without any ammonia; and potash remained in the tube.

Though these facts cannot be easily explained, except on the supposition that nitrogen is an oxide; yet (as is candidly acknowledged by Sir H. Davy), in processes so delicate and complicated, and involving such numerous data, we cannot be certain that every source of fallacy has been avoided, and every circumstance observed and

reasoned upon.

#### CHAPTER IX.

#### EARTHS.

THE term earth was, till lately, employed to denote "a tasteless; inodorous, dry, brittle, and uninflammable substance, not more than

five times heavier than water." This definition, however, was rendered imperfect by the discovery, that certain earths have a strong taste, and are readily soluble in water, which yet possess the other characters of earthy-bodies. Some of the earths were therefore removed from this class, and arranged among the alkalies. The classification, however, which appears to me most eligible, is that which divides them into earths simply, and alkaline earths; the latter partaking of the characters both of earths and alkalies. The alkaline earths are Barytes, Strontites, Lime, and Magnesia. The earths are Silex, Alumine, Zircon, Glucine, and Yttria\*.

Until the important æra of Sir H. Davy's discoveries, the earths were, with respect to the state of our knowledge, simple or elementary bodies. Many conjectures, it is true, had been formed respecting their nature; and, among these we find that their being composed of oxygen and a metallic base had been suggested as a probable theory. Led by the analogy arising from his experiments on the alkalies, Sir H. Davy, however, was the first to demonstrate what had before been only imagined; and to disunite, by the agency of strong electrical powers, the constituent principle of several of

this class of bodies.

In this part of the investigation, difficulties were encountered which demanded great perseverance and complicated processes. The affinity of the earthy bases for oxygen appears considerably to surpass that of the metals composing potash and soda; and it was found that simple exposure to the opposite electricities was not adequate to the separation of the principles which compose the earths; or, at least, that the effect was too indistinct to furnish satisfactory evidence of their nature. Sir H. Davy was, therefore, induced to electrify the earths, as he had formerly operated on potash, in contact with the oxides of known metals; with the expectation that the metallic base of the earth would unite with the metal contained in the oxide he employed, and form an alloy. Thus a mixutre of barytes and red oxide of mercury might be expected to yield an alloy of mercury with the metallic base of barytes; and such, in fact, was the result of the experiment; for a solid amalgam adhered to the negative wire, which, when thrown into water, evolved hydrogen, leaving pure mercury, and a solution of barytes. Mixtures of lime. strontites, or magnesia with oxide of mercury gave similar amalgams, from which the respective alkalies were regenerated by the action of air or water; but the quantity obtained was too minute for investigation.

On the suggestion of Professor Berzelius of Stockholm, the earths were next electrified negatively in contact with mercury itself; and in this way amalgams were obtained from barytes, strontites, lime, and magnesia. These compounds of mercury with the metallic base

† The reader may consult a history of opinions respecting the earths, in a note to Sir H. Davy's paper, Philosophical Transactions, 1808.

<sup>•</sup> The Agustine of Tromsdorff has been shown, by Berthollet, to be nearly Phosphate of Lime. Nicholson's Journal, 8vo. vii. 117.

of the earth decomposed water, and the earth, which had afforded them, was regenerated. Under naphtha, they might be preserved. for a considerable time; but at length they became covered with a

white crust of the regenerated earth.

To procure quantities of these amalgams sufficient for distillation, the earths were slightly moistened, and mixed with one third of red oxide of mercury: the mixture was then placed on a plate of platinum, a cavity was made in the upper part of it to receive a globule of mercury of from 50 to 60 grains in weight, and the whole was covered with a thin film of mercury; lastly the plate was made positive, and the mercury negative, by a proper communication with a battery of 500 pairs.

From these amalgams, the mercury was separated by distilling in small tubes of glass filled with the vapour of naphtha. Considerable difficulties, however, attended these operations; and after all, Sir H. Davy could, in no case, be absolutely certain, that there was not a small quantity of mercury in combination with the metals of

the earths.

The proportion of oxygen and metal has not yet been ascertained in any of the earths; but the evidence from analysis of their composition is perfectly satisfactory, the inflammable base appearing uniformly at the negative surface in the Voltaic circuit, and the oxygen

at the positive surface.

The decomposition of the other earths, alumine, silex, zircon, and glucine was not effected by the same means, that had been applied successfully to the alkaline earths. Combinations of potash and alumine, and of potash and silex, were electrified with the hope that the bases of these earths would be obtained in the state of an alloy with potassium. Soda and zircon were similarly treated. In all these cases, the phenomena indicated that some portion of the several earths had been decomposed; but in too minute a quantity to examine the

properties of their bases.

Lastly, potassium, amalgamated with about one third its weight of mercury, was electrified negatively under naphtha, in contact with the four earths, which were last enumerated. The potassium generated was thrown into water, and the alkali produced saturated with acetic acid. Now if any metal had thus been obtained from the earths. it would exist in the form of an alloy with potassium; both metals would be oxidized by the water; the potassium would reproduce potash, and the other metal the earth which gave it origin, which earth would be dissolved by the solution of potash, and would re-appear on adding an acid. The general tenor of the results gave great reason to conclude that alumine, silex, glucine, and zircon are, like the alkaline earths, metallic oxides.

By the use of the blow-pipe with compressed oxygen and hydrogen gases, Professor Clarke of Cambridge was led to believe that he had succeeded in effecting the decomposition of the earths, and in exhibiting their metallic bases in a separate form\*. The experiments,

<sup>\*</sup> Thomson's Annals. viii. 313, 357, 471; ix. 194. Journal of Science, &c. ü. 119.

however, have been frequently repeated in the laboratory of the Royal Institution, but always without success, though the heat obtained, was sufficient for the fusion of corundum, rock crystal, and other refractory bodies.\* It is probable, therefore, that Dr. Clarke may have been misled by the presence of some impurities in the earths, which were submitted to his experiments. But in a subsequent memoirt, he declares his conviction of the accuracy of his results to be strengthened by carefully repeated experiments in which a distinct metallic film was produced on the surface of barytes, and was found to give no traces of iron or zinc deposited (as had been suggested) by the hydrogen gas.

### SECTION I.

## Barytes.

Barytes may be obtained in a state of purity, by the calcination of its carbonate or nitrate, in a manner which will be hereafter described. (See chap. xi. sect. 4, art. iv.) It exhibits, when pure, the following properties:

I. Barytes, in a pure form, has a sharp caustic taste; changes vegetable blue colours to green; and serves as the intermedium between oil and water. In these respects, it bears a strong resemblance

to alkalies.

II. When exposed to the flame of the blow-pipe on charcoal, it melts; boils violently; and forms small globules, which sink into After being kept in fusion in a crucible during ten the charcoal. minutes, it still, according to Berthollet, contains 9 per cent. of water; from theory it should contain 10.59 per cent. This, however, is true only of barytes which has been obtained from the carbonate, by a process to be described hereafter. Barytes procured by decomposing the nitrate of that earth, is not fusible, and appears to contain little if any watert.

III. If a small quantity of water be added to recently prepared barytes, it is absorbed with great rapidity; prodigious heat is excited; and the water is completely solidified, a sort of hard cement being obtained. A little more water converts this mass into a light bulky powder; and, when completely covered with water, the barytes is dissolved. Boiling water should be employed for this purpose; unless sufficient temperature has been produced, by the sudden addition of the whole quantity necessary for solution.

IV. When the solution, prepared with boiling water, is allowed to cool slowly, it shoots into regular crystals. These have the form of flattened hexagonal prisms, having two broad sides, with two intervening narrow ones; and terminated, at each end, with a quadran-

† Nicholson's Journal, xxiii. 281.

Journal of Science, ii. 461. † Thomson's Annals, x. 133, 375.

gular pyramid. They lose, according to Bucholz, half their weight of water in a red heat; the barytes then continues fused, and parts with no more water, though still combined with the proportion above stated. Mr. Dalton, from his experiments, infers that the crystals contain 30 barytes and 70 water per cent., which would make them

consist of 1 atom of barytes + 20 atoms of water.

V. The crystals are so soluble, as to be taken up, when heated, merely by their own water of crystallization. When exposed to a stronger heat, they swell, foam, and leave a dry white powder, amounting to about 47 parts from 100 of the crystals. This again combines with water with great heat and violence. At 60° of Fahrenheit, an ounce measure dissolves only 25 grains of the crystals, i. e. they require for solution, 17 times their weight of water. Exposed to the atmosphere, they effloresce, and become pulverulent.

VI. When added to spirit of wine, and heated in a spoon over a

lamp, they communicate a yellowish colour to its flame.

VII. The specific gravity of this earth, according to Fourcroy, is 4; but Hassenfratz states it at only 2.374. The former account, however, is the more probable. All its combinations have considerable specific gravity; and hence its name is derived, viz. from the Greek word Bapus signifying heavy. The weight of its atom Mr. Dalton states at 68, but this number is probably rather too low, as will appear in the sequel.

VIII. Barytes does not unite with any of the alkalies.

Of the base of barytes or barium.—The base of barytes was obtained by Mr. Davy by distilling its amalgam, obtained in the follow-A quantity of native carbonate of barytes was made into a paste with water, and placed on a tray of platinum; a cavity was made in the paste to receive a globule of mercury, which was rendered negative, at the same time that the platinum was made positive by means of a Voltaic battery, containing about 100 double plates. In a short time, an amaglam was formed consisting of mercury and barium. This amalgam was introduced into a little tube made of glass free from lead, which was bent into the shape of a retort, then filled with the vapour of naphtha, and hermetically sealed. Heat was then applied to the tube, till all the mercury was driven off.

The residuum of this distillation was a dark grey metal, with a lustre inferior to that of cast iron. At the ordinary temperature of the air it remained a solid; but became fluid at a heat below redness. It did not rise in vapour, till heated nearly to redness, and then ac-

ted violently upon the glass,

When exposed to the air, this substance rapidly tarnished, and fell into a white powder, which was barytes. When this process was conducted in a small portion of air, the oxygen was absorbed; and the nitrogen remained unaltered. A portion of it thrown into water acted upon it with great violence, and sank to the bottom, producing barytes, and evolving hydrogen gas.

The quantities obtained were too minute for an examination either

of its physical or chemical qualities. It sank rapidly in water, and even in sulphuric acid, though surrounded by globules of hydrogen equal to two or thee times its volume. Hence it is probable that it cannot be less than four or five times as heavy as water. It was flattened by pressure, but required considerable force for this effect.

The proportion of the components of barytes Sir H. Davy deduces to be 89.7 barium and 10.3 oxygen per cent. The determination of

Berzelius nearly agrees with this, viz.

Barium, from the experiments of Gay Lussac and Thenard, appears capable of combining with a larger quantity of oxygen than exists in barytes; for when pure barytes, prepared from the nitrate, was heated in dry oxygen gas, the gas was rapidly absorbed, and the earth became grey, and appeared glazed on its surface.

On the supposition that barytes consists of an atom of barium united with an atom of oxygen, the atom of barium should weigh 64. and that of barytes 71.5. The second oxide probably contains an additional atom of oxygen; and its atom, in that case, will weigh

79.

### SECTION II.

#### Strontites.

I. STRONTITES (called also Strontia, from Strontian in Scotland, the place where it was first discovered, in combination with carbonic acid) resembles barytes in many of its properties; and all that is included in the first three paragraphs of the last section may be ap-

plied, also, to this earth.

II. Like barytes, strontites is readily soluble in boiling water; and the solution, on cooling, affords regular crystals; but the shape of these differs considerably from that of barytic crystals. The crystals of strontites are thin quadrangular plates; sometimes square, oftener parallelograms; not exceeding in length, and not reaching in breadth, a quarter of an inch. Sometimes their edges are plain, but they oftener consist of two facets, meeting together, and forming an angle like the roof of a house. They adhere to each other in such a manner as to form a thin plate, of an inch or more in length, and half an inch in breadth. Sometimes they assume a cubic form.

III. These crystals undergo, by the action of heat, much the same changes as those of barytes; and leave only about 32 per cent. of dry Vol. I.—D d

earth. One part of the crystals requires about 511 of water at the temperature of 60° for solution, but boiling water takes up half its weight. Mr. Dalton supposes the crystals to consist of 1 atom of strontites and 12 atoms of water.

IV. Boiling alcohol, with the addition of these crystals, burns

with a blood red flame.

V. Strontites does not combine with alkalies. Barytes has no affinity for it; for no precipitation ensues, on mixing the watery so-

lutions of the two earths.

From the preceding enumeration of its characters, it appears that strontites differs from barytes in the form of its crystals, which contain also more combined water, and are less soluble than those of barytes; and also in affording, with alcohol, a flame of different colour. These distinctions were deduced by Dr. Hope, from his excellent series of experiments on the two earths\*. Other circumstances of distinction, derived from the properties of their respective salts, will be stated hereafter.

Of the base of strontites or strontium.—Strontium may be procured by exactly the same process as barium, substituting the native carbonate of strontites for that of barytes. It was first obtained by Sir H. Davy in 1808, but in very minute quantities. It resembled barium, had not a very high lustre, was difficultly fusible, and not volatile. It was converted into strontites by exposure to air, or by contact with water.

The product of its oxidation, strontites, Sir H. Davy thinks probable is composed of 86 strontium and 14 oxygen. In this case, 45 would be nearly the weight of the atom of strontium, and 52.5 that of the atom of strontites. Stromeyer has lately deduced its campo-

sition to be.

Strontium . . . . . . . . 84.669 or 100.000 Oxygen . . . . . . . . . . 15.331 18.107

100.

And, taking with Dr. Wollaston, 10 is the equivalent of oxygen, he makes the number for strontium to be 55.2, and for strontites 65.2?

### SECTION III.

#### Lime.

I. Its external qualities.—These may be exhibited in common quicklime, such as is employed for the purpose of building or agri-

<sup>\*</sup> See Edinburgh Transactions, vol. iv. † Ann. de Ch. et Ph. iii. 397.

culture. In the same state, it is sufficiently pure, for demonstrating its chemical properties; but, when used for purposes of the latter kind, it should be fresh burnt from the kiln. For accurate experiments, it should be prepared by calcining Carara or Parian marble in a crucible for several hours. Its specific gravity is 2.3. It requires an intense heat for its fusion, and is not volatile.

II. Relation of lime to water.

(a) Lime absorbs water very rapidly with considerable heat and noise. This may be shown by sprinkling a little water on some dry quicklime. The above-mentioned phenomena will take place, and the lime will fall into powder, which has been called hydrate of lime. In this compound, the lime is to the water, according to Mr. Dalton, as 28 to 8; according to Davy, as 55 to 17; and to Berzelius, as 100 to 32.1. Some care, however, is necessary in its preparation, lest more water should be added, than is essential to its constitution. It affords a very convenient form of keeping lime, for occasional use in a laboratory; for the hydrat may safely be preserved in glass bottles, which are almost constantly broken by the earth in its perfectly dry state. The hydrat of lime differs from those of barytes and strontites, in retaining its water much less forcibly; for the whole of it may be expelled by a strong red heat.

The degree of heat, produced by the combination of lime with water, is supposed by Mr. Dalton to be not less than 800°, and is sufficient to set fire to some inflammable bodies; and when a large quantity of lime is suddenly slacked in a dark place, even light, according to Pelletier, is sometimes evolved. The caloric, which is thus set at liberty, is doubtless that contained in the water, and essential to its fluidity. By combination with lime, water passes to a solid state, and probably even to a state of much greater solidity than that of ice. Hence, during this change, it evolves more caloric than during conversion into ice; and hence even ice itself, when mixed with quicklime, in the proportion of one to two, enters into a combination which has its temperature raised to 212°. When a sufficient quantity of water has been added to reduce lime into a thin liquid, this is

called milk or cream of lime.

Lime is, in some degree, convertible into vapour, by combination with water. When a piece of moistened paper, stained with the juice of the violet, is held in the steam, which arises from lime suddenly slaked, its colour is changed from blue to green. Hence the smell which is perceived during the slaking of lime.

(b) Lime absorbs moisture from the atmosphere, and falls gradually into powder, containing pure lime and water, in the proportion

nearly of 100 to 32.

(c) Lime is very sparingly soluble in water, viz. in the proportion of about 1 to 500; according to Thomson, 1 to 758; to Davy, 1 to 450; and to Dalton, at 60° Fahrenheit, 1 to 778. The experiments of Mr. Dalton tend to establish a curious fact respecting the solubility of lime, viz. that it dissolves more plentifully in cold than in hot water. He has given the following table, the first column of which expresses the temperature of the water; the second, the num-

ber of grains of water, required to take up one grain of lime; and the third, the number required to dissolve one grain of hydrate of lime.

Temperature.			olve	Grains of water that dissolve I gr. of Hydrate.				
60°				584				
130°		 97	2	720				
				952				

At the freezing point, or nearly so, Mr. Dalton thinks it probable that water would take up nearly twice as much lime, as is dissolved

by boiling water.

Lime, when thus dissolved, forms what has been termed lime-water. This solution tastes strongly of lime, turns vegetable blues to green, and unites with oil, forming an imperfect soap. To prepare the solution, lime is to be slaked to a thin paste, and a sufficient quantity of water afterwards added. The mixture is to be stirred repeatedly, the lime allowed to settle, and the clear liquor decanted for use. It must be preserved in closely stopped vessels, for reasons which will

be stated in the chapter on carbonic acid.

(d) When lime water is freely exposed to the atmosphere, the lime is precipitated from it in the state of a carbonate; and it is, therefore, not possible to obtain crystals of pure lime, by evaporating lime water in the common way. Its crystallization, however, has been effected by Gay Lussac, by inclosing a vessel of lime water, and another of concentrated sulphuric acid, under the same glass receiver\*. The evaporation of the water goes on quickly, especially when the sulphuric acid is occasionally renewed, and small transparent crystals are obtained in regular hexahedrons, cut perpendicularly to their axes. They remain transparent when exposed to the air for a few days, and are then changed into carbonate of lime. By ignition in a glass tube, their water of crystallization is expelled, and they are proved to consist of

Lime . . . . . . . . 76.26 . . . . . . . 100
Water . . . . . . 23.74 . . . . . . . . 31.14

100.

These crystals agree, therefore, very nearly in composition with the hydrate (or hydroxure, as Gay Lussac proposes to call it) which is obtained by exposing quicklime to a damp atmosphere. This, if the atom of water be taken at 8.5, would make the atom of lime 26.5, and that of the hydrate 35. Or, taking oxygen with Dr. Wollaston as 10, and the equivalent of water to be 11:32, the equivalent of lime will be 35.46, and that of the hydrate 46.78.

Lime does not combine, in any notable proportion, with the alka-

lies or earths already described, except by fusion.

The base of lime, to which Sir H. Davy has given the name of calcium, he has never been able to examine, exposed to air or under naphtha. In the case, in which he was able to distil the quicksilver

<sup>\*</sup> Ann. de Chim. et Phys. i. 334.

from its amalgam, to the greatest extent, the tube unfortunately broke whilst warm; and, at the moment that the air entered, the metal, which had the colour and lustre of silver, instantly took fire,

and burnt, with an intense white light, into lime.

There appears to be only one compound of calcium and oxygen, viz. lime; and, in this, the oxygen is to the metal, according to Sir H. Davy, as 7.5 to 20. Berzelius electrified lime liquor in contact with mercury, and obtained an amalgam of mercury with calcium. On this, water was made to act; and, from the quantity of lime that was formed, he estimated its composition to be,

100 139.4

This would make the atom of calcium to weigh 20, and the atom of lime 27.5, and of the hydrate 36.

## SECTION IV.

## Magnesia.

MAGNESIA possesses the properties of an alkali, but in a considerably less degree than any of the foregoing earths. Its characters are as follow:

I. When perfectly pure, it is entirely destitute of taste and smell.

Its specific gravity is between 2 and 3.

II. No heat is excited by the affusion of water, and only a very small proportion, not exceeding a 2000th its weight, of earth is dissolved. Magnesia appears, however, to have some affinity for water; for when moistened, and afterwards dried, its weight is found increased in the proportion of 118 to 100. When precipitated by pure potash or soda from any of its salts, it falls down in union with water as a hydrate, which, when dried by a very gentle heat; forms transparent masses. In this state, according to Day, it contains about 1 of its weight of water; or, according to Berzelius, 100 parts of magnesia absorb from 142 to 144 of water.

III. Magnesia changes to green the blue colour of the violet; but the watery solution of magnesia, when filtered through paper, does not produce a similar effect. In this respect it differs from lime. It

reddens turmeric like the alkalies.

IV. It is not dissolved by liquid alkalies, nor by alkaline earths; and in the dry way, it has no affinity for barytes or strontites.

The base of magnesia, for which Sir H. Davy has proposed the term magnesium, is but imperfectly known. In the attempts to distil its amalgams, the metal seemed to act upon the glass, even before the whole of the quicksilver was distilled from it. In one experiment, in which the process was stopped, before the mercury was en-

tirely driven off, it appeared as a solid, having the same whiteness and lustre as the other metals of the earths. It sunk rapidly in water, though surrounded by globules of gas, and produced magnesia. In the air, it quickly changed, becoming covered with a white crust, and falling into a white powder, which proved to be magnesia. This earth Berzelius states, in round numbers, to consist of 38 or 39 per cent. oxygen, and 61 or 62 magnesium.

## SECTION V.

### Silex.

I. Siliceous earth, or silex, may be obtained tolerably pure from flints by the following process:—Procure some common gun-flints, and calcine them in a crucible in a low red heat. By this treatment they will become brittle, and easily reducible to powder. Mix them, when pulverized, with three or four times their weight of carbonate of potash, and let the mixture be fused in a strong red heat, in a The materials must bear only a small proportion to the capacity of the crucible; and the heat must at first be very moderate, and slowly increased. Even with this precaution, the mass, on entering into fusion, will be apt to overflow; and must be pressed down as it rises, by an iron rod. When this effervescence has ceased, let the heat be considerably raised, so that the materials may be in perfect fusion during half an hour, and pour the melted mass on a copper or iron dish. We shall thus obtain a compound of alkali and siliceous earth. Dissolve this in water, filter the solution, and pour it into diluted sulphuric or muriatic acid. An immediate precipitation will ensue, and, as long as this continues, add fresh portions of the solution. In precipitating the alkaline solution of silex, more acid must be used than is sufficient to engage the alkali; and the alkaline liquor must be added to the acid, and not the reverse; for, in the latter case, the precipitate will be glass, and not silex. Let the precipitate subside, pour off the liquor that floats above it, and wash the sediment with hot water, till it comes off tasteless. Then dry it.

Silex, obtained by this process, though pure enough for the following experiments, may still contain a portion of alumine. To separate the latter earth, boil the precipitate with diluted sulphuric acid, to which a little sulphate of potash may be added. The alumine will thus be dissolved; and the silex may be freed from the solution of alum by repeated washings with water. Even silex, however, that has been most carefully washed, still gives traces of potash on the application of electric above in a power.

application of electro-chemical powers. (Davy.)

II. Siliceous earth, as thus obtained, has the following qualities:
(a) It is perfectly white and tasteless. It is infusible by the intense heat of Voltaic electricity\*, but was melted by Dr. Clarke

<sup>\*</sup> Phil. Trans. 1815. p. 370.

with the oxygen and hydrogen blow-pipe. To a certain degree it appears to be volatile, for a filamentous substance, collected from iron furnaces, resembling amianthus, was found by Vauquelin to be pure silex.

(b) When mixed with water, it does not form a cohesive mass like alumine, and has a dry and harsh feel to the fingers. It retains, when fresh precipitated, about 26 per cent. of water, after being dried at 70° Fahrenheit. But, according to Berzelius, this water is not chem-

ically combined.

'(c) It is insoluble in water. Yet, when fresh precipitated, water has the property of retaining in solution about one thousandth of its weight\*. That silex, however, is dissolved in water by processes of nature, can scarcely be doubted, when it is considered, that it is

found, in considerable quantities, in a crystallized form.

(d) It is not acted on by any acid, except the fluoric. Sulphuric acid poured on this compound, according to Dalton, expels the fluoric acid, but does not unite with the silex. But though the earth itself is not dissolved by acids, yet when first combined with an alkali, it unites with several acids, forming triple saltst. When fresh precipitated, however, Dr. Marcet asserts, that it is sparingly soluble in most acids; and, for this reason, he recommends, in analysis, to precipitate silex by muriate of ammonia, which does not, like the acids, redissolve it.

(e) When prepared in the foregoing manner, and very minutely divided, silex is taken up by a solution of pure potash, or of soda, but not by ammonia. In the aggregated state of flints, however, it is perfectly insoluble in this way by alkaline solutions; an excellent illustration of the principle that a very minute division of solid bodies, by presenting a greater surface to the action of fluids, facilitates so-

lution.

(f) When mixed with an equal weight of carbonate of potash, and exposed to a strong heat in a furnace, it forms a glass, insoluble in water, and identical in all its properties with the glass commonly manufactured. It is owing to the siliceous earth which it contains, that glass is decomposed by the fluoric acid. Glass, however, has accasionally other ingredients, besides the two that have been men-

tioned‡.

(g) With a larger proportion of alkali, as three or four parts to one of silex, this earth affords a compound called by Dr. Black, silicated alkali. This compound, formed by the process which has been just described, is soluble in water, and affords a good example of the total change of the properties of bodies by chemical union; for, in a separate state no substance whatever is more difficult of solution than silex. The solution of silicated alkali was formerly termed, liquor silicum, or liquor of flints. Acids seize the alkali, and precipitate the silex, which is even separated by mere exposure to the atmos-

<sup>\*</sup> See Klaproth's Contributions, i. 399, 400. † 81 Ann. de Chim. 239. ‡ See Guyton, Ann. de Chim. vol. lxxiii.

phere, in consequence of the absorption of carbonic acid by the alkali. Without attention to the circumstances mentioned in speaking of its preparation, glass, and not silex, is separated by acids\*.

(h) Barytes, or strontites, and silex combine together, in a manner similar to the union of this earth with alkalies; but the combina-

tion has not been applied to any useful purpose.

(i) When a solution of silex in potash is mingled with one of barytes, of strontites, or of lime in water, or of alumine in alkali, a precipitation ensues. Hence silex may be inferred to have an affinity for all these earths, in the humid way. The composition of these

precipitates is stated by Mr. Dalton in his System, p. 541.

In consequence of its possessing a stronger affinity for alkalies and earths than for acids, as well as from its other habitudes, silex has been thought to present a closer analogy with acids than with earths, and in a chemical arrangement to be more properly placed in the former class, than in the latter. On the other hand, as it is deficient in some of the characters which have hitherto been deemed essential to acidity, I have not thought it expedient to remove it from the place which it has hitherto held in chemical arrangements.

Base of Silex.—In his attempts to obtain the base of silex, or silicium, in a state of separation, Sir H. Davy has hitherto been unsuccessful; though the results of his experiments leave little room to

doubt that this earth is, like the rest, a metallic oxide.

Berzelius decomposed silex, by fusing it with charcoal and iron in a blast furnace. He obtained an alloy of iron and silicium, which, by the action of a diluted acid, gave more hydrogen than the same weight of iron. This process was successfully repeated by Stromheyer, and the properties of the different alloys investigated. He recommends the fusion of 7 parts of iron, 5 of silex, and from  $\frac{1}{4}$  to  $\frac{3}{5}$  ths of a part of soot. From the results of acting on the alloy by dilute acids, Berzelius infers silex to consist of

Silicium Oxygen					
		100.			917.38

And Sir H. Davy deduces the proportions to be 31 of metal to 30 oxygen. These numbers, however, can be considered in no other light than as approximations; but since, according to recent experiments;, three parts of potassium are required to decompose one of silex, that earth cannot contain much less than half its weight of oxygen. The base, Sir H. Davy now believes not to be a metal but a substance most resembling boron; and like it, bearing an analogy to charcoal, sulphur, and phosphorus.

<sup>\* 81</sup> Ann. Ch. 179. See also his account of an attempt to analyze silica, in 40 Phil. Mag. 201.

<sup>†</sup> See Dalton, p. 538.

<sup>#</sup> Phil. Trans. 1814, p. 67.

### SECTION VI.

## Alumine.

I. Alumine may be obtained free from other earths, but still combined with carbonic acid, by precipitating a solution of alum in water by the bi-carbonate of potash. To secure its complete purification from sulphuric acid, Guyton advises that the precipitate be re-dissolved in nitric acid, that nitrate of barytes be cautiously added to the solution, till it no longer occasions milkiness, and that the alumine be afterwards precipitated, or separated from the nitric acid by heat\*. Electro-chemical analysis, however, in this as in many other instances, shows the imperfection of the common methods of separating bodies from each other; for the most carefully prepared alumine yields the metals of soda and potash, when negatively electrified in contact with mercuryt. Berzelius, also, found that when alumine is precipitated either from the sulphate or nitrate, it is contaminated with those acids; but not with the muriatic, when thrown down from the muriate of alumine by ammonia. Gay Lussac recommends the preparation of alumine by exposing that kind of alum which has ammonia for its base, first to a gentle heat to expel the water of crystallization, and afterwards to a red heat, which leaves the alumine

II. Alumine has the following properties:

- 1. It is destitute of taste and smell.
- 2. When moistened with water, it forms a cohesive and ductile mass, susceptible of being kneaded into a regular form. It is not soluble in water; but retains a considerable quantity, and is, indeed, a hydrate, containing, when dried at the temperature of the atmosphere, almost half its weight of water. Even after ignition, alumine has such an affinity for moisture, that it can hardly be placed on the scale, without acquiring weight. Berzelius found that 100 parts of alumine, after being ignited, gained 15½ from a dry atmosphere, and 33 from a humid one. For full saturation, 100 grains of alumine, he ascertained, require 54 of water§.

3. It does not affect blue vegetable colours.

4. It is dissolved by the liquid fixed alkalies, and is precipitated by acids unchanged. In ammonia, it is very sparingly soluble. It is not soluble in alkaline carbonates.

5. Barytes and strontites combine with alumine, both by fusion and in the humid way. In the first case, the result is a greenish or bluish coloured mass. In the second, two compounds are formed. The first, containing an excess of alumine, is in the state of an insoluble powder; the other, having an excess of the alkaline earth, re-

<sup>\*</sup> Ann. de Chim. xxxii. 64.

<sup>†</sup> Davy, Philosophical Transactions, 1808.

<sup>‡</sup> Ann. de Chim et Phys. v. 101.

<sup>§ 82</sup> Ann. de Chim. 14.

mains in solution. Alumine may be united, by fusion, with the fixed alkalies, and with most of the earths.

6. Alumine, as will be afterwards shown, has a strong affinity for

colouring matter.

7. Alumine has the property of shrinking considerably in bulk, when exposed to heat, and its contraction is in proportion to the intensity of the heat applied. On this property is founded the pyrometer of Wedgwood, which measures high degrees of heat, by the amount of the contraction of regularly shaped pieces of china clay. The pieces of clay are small cylinders, half an inch in diameter, flattened on the under surface, and baked in a low red heat. contraction of these pieces is measured, by putting them between two fixed rulers of brass or porcelain, twenty-four inches long, half an inch distant from each other at one end, and three tenths of an inch at the other. The rulers are divided into 240 equal parts, called degrees, which commence at the wider end; and each of which is equal to 130° of Fahrenheit. When the clay piece is fixed in its place, before exposure to heat, it is stationary at the first degree, which indicates about 1077° of Fahrenheit. After being strongly heated, in a small case which defends it from the fuel, its bulk is diminished, and it slides down, between the converging rulers, till stopped by their approach. The number on the graduated scale, opposite to the upper end of the piece, indicates the degree of heat to which it has been exposed. In the appendix, rules may be found for reducing the degrees of Wedgwood's pyrometer to those of Fahrenheit's thermometer. It is proper, however, to remark that this instrument is a much less accurate measurer of heat than was long supposed; and that its contraction is influenced not merely by the degree of heat to which it is exposed, but by the mode of its application.

Almost every thing that has been said respecting the base of silex is true, also, of that of alumine; for Sir H. Davy attempted the decomposition of the two earths by much the same processes. All that his results afford, is a strong presumption that alumine is a metallic oxide; but its base, alumium, has not yet been obtained in such a state as to make it a fit object of investigation. Yet alloys have been formed, which give sufficient evidence of its existence; and the presence of oxygen in alumine is proved, by its changing potassium into potash, when ignited with that metal.

## SECTION VII.

#### Zircon.

I. This earth was discovered by Klaproth in the year 1789, in a precious stone from the island of Ceylon, called Jargon or Zircon; and has since been detected in the hyacinth. It may be obtained by the following process:

Reduce the hyacinth to fine powder, which may be done in an agate mortar, after previously igniting the stone, and plunging it into cold water, to render it brittle. Mix the powder with nine times its weight of pure potash; and project it, by a spoonful at once, into a red-hot crucible, taking care not to add fresh portions till the former ones are melted. When the whole is in fusion, increase the heat for an hour, or an hour and a half. When the crucible has cooled, break it, and detach its contents; reduce them to powder, and boil them with distilled water. Let the insoluble part subside; decant the clear liquor, and wash the sediment with water, till the washings cease to precipitate muriated barytes. On the residuum pour muriatic acid to excess, and boil it during a quarter of an hour, filter the liquor, and evaporate to dryness in a leaden vessel. Redissolve the dry mass; filter again, and precipitate the zircon with carbonate of soda. The carbonate of zircon is thus obtained, from which the carbonic acid may be expelled by calcination.

II. Zircon has the following properties:

1. It has the form of a fine white powder, which has somewhat of the harsh feel of silex, when rubbed between the fingers. It is entirely destitute of taste and smell. Its specific gravity exceeds 4.

2. It is insoluble in water; yet it appears to have some affinity for that fluid, for it retains, when slowly dried after precipitation, one third its weight, and assumes a yellow colour and slight transparency, like that of gum arabic.

3. It is insoluble in pure liquid alkalies; nor, does it even combine with them by fusion; but it is soluble in alkaline carbonates. In the foregoing process, therefore, the carbonate of soda should not be added to excess.

4. Exposed to a strong heat, zircon fuses, assumes a light grey colour; and such hardnesss, on cooling, as to strike fire with steel, and to scratch glass, or even rock crystal.

5. Its action on other earths has not been fully investigated.

6. It is precipitated from its solutions in acids by triple prussiate

of potash\*.

III. The base of zircon, or zirconum, is still unknown, though investigated by Sir H. Davy in the same manner as the base of silex. When potassium was brought into contact with ignited zircon, potash was formed, and dark metallic particles were diffused through the alkali.

## SECTION VIIL

#### Glucine.

1. This earth was discovered by Vauquelin, in the year 1798. He obtained it from the aqua marina or beryl, a precious stone of a green colour, and very considerable hardness, which is found crystallized in Siberia. Glucine has since been detected in the emerald of Peru, and in the gadolinite. The following process may be employed to separate it from the beryl:

Klaproth, ii. 214.

Let the stone, reduced to a fine powder, be fused with three times its weight of pure potash. To the fused mass add a quantity of water, and afterwards diluted muriatic acid; which last will effect a complete solution. Evaporate the solution to dryness, re-dissolve the dry mass, and add carbonate of potash so long as any precipitation ensues. Dissolve the precipitate in sulphuric acid; add a little sulphate of potash; and, on evaporation, crystals of alum will be obtained. By this process the alumine is detached. The residuary liquor, which yields no more crystals, contains the glucine, and a small portion of alumine. Add a solution of carbonate of ammonia to excess; this will throw down the alumine, and the glucine will remain dissolved by the superabundant carbonate. When this solution is evaporated to dryness, and moderately heated, the alkaline carbonate is expelled, and a carbonate of glucine remains, in the proportion of 16 parts from every 100 parts of the stone.

II. Glucine has the following properties:

1. It is a fine white and soft powder, resembling alumine in its sen ble properties; and like that earth, adhering to the tongue. Its specific gravity is 2.97.

2. It has no action on blue vegetable celours.

3. It does not harden, or contract, like alumine, by heat; and is infusible.

4. It is insoluble in water, but forms with it a ductile paste.

It is soluble in liquid potash and soda, but not in the solution of pure ammonia. In these respects it agrees with alumine.

6. Glucine is soluble in carbonate of ammonia; a property distin-

guishing it from alumine.

7. It appears like alumine, to have an affinity for colouring

matter.

8. With the different acids it forms combinations, which have a sweet and rather astringent taste. Hence its name has been derived from pauce signifying sweet.

9. It is not precipitated by triple prussiate of potash.

III. We have no knowledge of the base of glucine. When obtained, its proper denomination will be glucinum. The general fact of its existence is proved by igniting glucine with potassium, which is thus changed into potash.

#### SECTION IX.

# Yttria, or Ittria.

1. This earth was discovered in 1794, by Professor Gadolin, in a stone from Ytterby in Sweden; and its title to the character of a peculiar earth rests, also, on the unquestionable authority of Klaproth and Vauquelin, both of whom have made it the subject of experiment. The following process for obtaining it, is described by Vauquelin in the 36th volume of the Annales de Chimie, p. 150.

Fuse the pulverized stone (called Gadolinite) in the manner already described, with twice its weight of potash; wash the mass with boiling distilled water, and filter. The filtered solution, which has a beautiful green colour, yields, during evaporation, a black precipitate of oxide of manganese. When this has ceased to appear, allow the liquor to stand; decant the clear part, and saturate with nitric Let the insoluble part be, also, digested with extremely dilute nitric acid, which will take up the soluble earths only, and will leave, undissolved, the silex and oxide of iron. Let the two portions be mingled together, and evaporated to dryness; then re-dissolved and filtered: by which means any remains of silex and oxide of iron are separated. To obtain the yttria from the nitric solution, it would be sufficient, if no other earth were present, to precipitate it by carbonate of ammonia; but small portions of lime, and of exide of manganese, are still present along with it. The first is separated by a few drops of carbonate of potash; and the manganese, by the cautious addition of hydro-sulphuret of potash. The yttria is then to be precipitated by pure ammonia, washed abundantly with water, and dried. It amounts to about 35 per cent. of the stone.

II. Yttria has the following properties:

1. It is perfectly white; but it is difficult to preserve it free from a slight tinge of colour, owing to its contamination with oxide of manganese.

2. It has neither taste nor smell; and it is smooth to the touch,

like alumine.

3. It is insoluble in water, and infusible except by an intense heat.

4. It is very ponderous; its specific gravity being 4.842.

5. It is not attacked by pure alkalies; and, in this respect, it differs from glucipe and alumine, both of which are abundantly soluble in fixed alkalies.

6. Like glucine, it is soluble in carbonate of ammonia, but five or six times less so than that earth; or, in other words, of equal quantities of glucine and yttria, the latter requires for solution five or six times more of the carbonate of ammonia than the former.

7. It is soluble in most acids; and is precipitated by pure alka-

lies, by barytes, and by lime.

8. From these solutions it is also precipitated by the oxalic acid, and by oxalate of ammonia, in a state resembling fresh precipitated muriate of silver. Prussiate of potash throws it down in small white grains passing in a short time to pearl grey; phosphate of soda in a white gelatinous form; and infusion of galls in brown flocculi.

9. Yttria, which has been a long time exposed to the action of fire, gives out chlorine gas, when dissolved in common muriatic acid;

thus manifesting one property of a metallic oxide\*.

III. The base of yttria has not yet been exhibited in a separate form; but the presence of oxygen in yttria is established by its converting potassium into potash, when ignited with that metal.

<sup>\*</sup> Nicholson's Journal, xviii. 77.

#### SECTION X.

### Thorina.

I. WHILE analyzing some minerals from the neighbourhood of Fahlun in Sweden, Professor Berzelius found in them a new earth, which he had also extracted, in the summer of 1815, from a species of gadolinite. In these it was combined with the fluate of cerium and yttria. The pulverized mineral was first treated with concentrated sulphuric acid, which decomposed the greater part of it, and expelled the fluoric acid. From this solution, sulphate of potash precipitated the oxide of cerium, and caustic ammonia afterwards occasioned a farther precipitate. This, dissolved by long digestion in muriatic acid, consisted of the muriates of yttria and of the new earth. It was evaporated to dryness, in order to expel the excess of acid, and water poured over it to dissolve the muriate of yttria. The residue was subjected to the action of muriatic acid, and the solution accurately saturated by caustic ammonia. On adding water, and applying a boiling heat, a white gelatinous precipitate fell, which was collected on the filter. The liquor, that passed through the filter, was again saturated with pure ammonia, and heated to ebullition, which occasioned a fresh precipitation of the same earth. This, when washed and gently dried, is the substance in question.

II. 1. This earth, when dried, is perfectly white; it absorbs carbonic acid, and dissolves with effervescence in acids. After calcination, its white colour remains unimpaired; but if the heat has been strong, it is rendered less easily soluble in acids. The neutral solutions of it have a purely astringent taste, which is neither sweet, nor saline, nor bitter, nor metallic, a property in which it differs from all

the earths except zirconia.

2. When dissolved in a slight excess of sulphuric acid, and subjected to evaporation, it yields transparent crystals, which are not altered by exposure to the air, and have a sweet astringent taste.

3. It dissolves readily in nitric and muriatic acids, but does not afford crystallizable salts. When precipitated by pure alkalies, it absorbs carbonic acid from the air with avidity; and the alkaline carbonates throw it down, in combination with the whole of their carbonic acid. It is precipitated by the oxalate, tartrate, and benzoate of ammonia. Succinate of ammonia occasions a precipitate, which is immediately re-dissolved; and ferro-prussiate of potash throws down a white precipitate, which is soluble in muriatic acid.

4. It is not soluble, even when freshly precipitated and at a boiling temperature, by the pure alkalies. The alkaline carbonates dissolve it, but much more sparingly than any other earth on which

they are capable of acting.

5. It is not reducible, when strongly heated in contact with charcoal. Before the blow-pipe, it cannot be brought into fusion. With borax or phosphate of soda, it fuses into a transparent glass, but is infusible with soda.

Messrs. Gahn and Berzelius having been accustomed to speak of this earth under the name of Thornia (from Thor, a Scandinavian deity), we may distinguish it by this name, till a more appropriate

one shall be pointed out.

Thorina differs from the other earths in the following properties: From alumine and glucine, by its insolubility in liquid potash; from ystria, by its solutions being purely astringent to the taste, without any sweetness, and by the property of being precipitated at a boiling heat, except when prevented by too great an excess of acid. It differs from zirconia in the following respects: 1st, Because, after being ignited, it is still soluble in acids. 2d, It is not precipitated by sulphate of potash, which throws down zirconia, even from solutions containing a considerable excess of acids. 3d, Thornia is precipitated by oxalate of ammonia, which is not the case with zirconia. 4th, Its combination with sulphuric acid crystallizes readily, while sulphate of zirconia forms, when pure and dried, a gelatinous mass, without any trace of crystallization.

## CHAPTER X.

#### OF ACIDS IN GENERAL.

THE term acid is applied to all bodies that possess one or more

of the following properties.

1. The acids have a peculiar taste, which is expressed in common language by the term sourness. This is very different, as to its degree, in different acids. In some it is so intensely strong, that they cannot be applied to the tongue without producing pain; and it characterizes them, even when diluted with several hundred times their weight of water. The sourness of others is such only, as to render them agreeable to the palate.

2. The acids redden blue vegetable colours; and they possess this property even when greatly diluted. Hence blue vegetable infusions, or papers stained with them, become tests of the presence of uncombined acids. A single drop of sulphuric acid is capable of reddening a large quantity of water coloured with litmus, or with

syrup of violets.

3. The acids combine chemically with alkalies, earths, and metallic oxides; and totally destroy the peculiar qualities of those bodies. Let a few ounce-measures of water be tinged blue with syrup of violets; add a few drops of solution of potash, and the colour will be changed to green; then drop in, very slowly and cautiously, sulphuric acid much diluted, and the blue colour will be restored. At this point, neither the acid nor the alkali is in excess, as they are said to neutralize each other; and, on farther examination, it will be found that the other characteristic qualities of the components have ceased to be apparent in the compound.

It is not necessary, however, in order to entitle a body to rank

among the acids, that it should possess all the qualities which have been enumerated. The prussic acid, for example, is neither sour to the taste, nor does it redden blue vegetable colours; but yet, from its manifesting the properties of chemical combination, enumerated under the third head, it is arranged among the acids. Other bodies, again, are excluded (though perhaps improperly) from this class, which possess, partly, the characters of acids. Thus sulphureted hydrogen changes the blue colours of vegetables to red; and combines chemically with alkalies and earths.

All the acids were inferred by Lavoisier, from analogy with those which had already been decomposed, to contain oxygen, which was considered, by that distinguished philosopher, as the general principle or cause of acidity. Since the brilliant discoveries of Sir H. Davy, we may, with equal justice, consider oxygen as the general principle of alkalinity. And besides, it has been lately proved with respect to tellurium and to the new substance iodine, and has been rendered highly probable with respect to chlorine, that these bodies afford acids, not only by uniting with oxygen, but also by combining with hydrogen. Sulphur, also, by combination with hydrogen, acquires many characters of an acid; and a compound base of carbon and nitrogen, called cyanogen, has been shown by Gay Lussac to form prussic acid by the addition of hydrogen. The theory, therefore, that oxygen is essential to acidity, must be abandoned. But it is still important to know that most of the acids contain oxygen; because it explains many of their most interesting qualities, depending on the transfer of oxygen from the acids to the bodies on which they act.

The peculiar properties of each acid are derived from the combustible base, with which the oxygen is united; and so, also, is its specific name. Thus sulphur, when oxygenated, affords sulphuric acid; carbon, carbonic acid; and so of the rest. But the same combustible base admits of being combined with different proportions of oxygen; and the compounds, thus generated, are distinguished by a very different train of qualities. Sulphur, for example, when combined with the full proportion of oxygen, with which it is capable of uniting, affords a very dense and corrosive acid, called the sulphuric; when oxygenated in a less degree, it yields a penetrating and suffocating gas called the sulphurous acid. By these two terminations, the degree of oxygenation are distinguished. Thus we have the phossphoric and phosphorous acids, the nitric and nitrous; the termination ic denoting an acid with its full proportion of oxygen. In some cases, a combustible base, which affords an acid when fully oxygenated, constitutes only an oxide when combined with a less quantity of oxygen. Carbon, for example, affords carbonous oxide and carbonic acid, but

so far as is hitherto known, no intermediate product.

The following table exhibits the compounds, which result from the oxygenation of the principal combustible bases. It is introduced in this place, chiefly to show that the oxygen in the more highly oxygenized compounds is in quantities, which are simple multiples, of those in the less oxygenized compounds.

100 parts of		united with	Result.			
Carbon	<b>§</b> 265		carbonic acid.			
, , , , , , , , , , , , , , , , , , ,	<b>(</b> 132)		carbonous oxide.			
	150		sulphuric acid.			
Sulphur {	₹ : 100		. sulphurous acid.			
	50		persulphurous acid?			
	285	oxygen	nitric acid.			
Nitrogan	228		nitrous acid.			
Nitrogen \	) 114		nitric oxide.			
	L 57		nitrous oxid <b>e.</b>			
Phosphorus	ς 135	oxygen	phosphoric acid. phosphorous acid.			
rnospnorus	<b>2 67.</b> 5		phosphorous acid.			

It is in consequence of the oxygen, which they contain, that several of the acids are decomposed by inflammable substances, with the disengagement of intense heat and light; or that the acids are (as they have been termed by Dr. Thomson) supporters of combustion. This property belongs most remarkably to those acids, in which oxygen is most weakly combined. Thus the nitric acid retains its oxygen so feebly, that many inflammable substances, when merely introduced into it at the ordinary temperature of the atmosphere, take fire and burn with vehemence. It is not, however to be understood that oxygen, and the compounds into which it enters, are the only supporters of combustion, for chlorine, iodine, and probably fluo-

rine, belong also to the same class of bodies.

All acids in a solid or liquid state, it has been observed by Berzelius, contain water as an essential element, and do not abandon it without decomposition. Sulphuric and nitric acids, for example, cannot exist independently of water. In acids that are capable of assuming a solid form, water appears to exist in two states, as a base essential to the constitution of the acid, but yet incapable of neutralizing its acid properties; and as water of crystallization. Thus the citric acid in crystals contains 21 per cent. of water, of which only one third can be expelled by heat without destroying the acid. A different view, however, of this subject has been lately taken by Dr. Murray\*, who considers the oxygen and hydrogen in all acids which are thus constituted, as existing, not in the state of water, but of ternary combination with the elements of the acid, and as together conferring acidity. For example, liquid sulphuric acid he regards not as a compound of real sulphuric acid and water, but as a ternary compound of sulphur, oxygen, and hydrogen. Acidity, it would appear, therefore, which is sometimes dependant on oxygen, and sometimes on hydrogen, is in other cases (and those often of acids of a high degree of intensity), the result of the combined operation of the two principles.

Every acid, with a few exceptions, is capable of uniting with each individual of the classes of alkalies, earths, and metallic oxides. In these compounds, the separate qualities of the component princi-

<sup>\*</sup> See his paper on muriatic acid. Edinburgh Trans.

ples are in many instances no longer apparent, and hence they have been called neutral salts. In every salt, then, there are present two distinct ingredients. The acid, of whatever kind it may be, has been denominated, by Lavoisier, the salifying principle; and the body, with which the acid is combined, whether an alkali, an earth, or an oxide of any of the common metals, the salifiable base, or simply the base. The salts, formed by an individual acid with all these different bases, may be considered as a genus or class; and may be distinguished by a generic name, expressive, in part, of their composition. This generic name is taken from that of the acid. The combination of sulphuric acid, for instance, with any base, is called a sulphat or sulphate; of phosphoric acid a phosphate; and so of the rest. The name of the individual salt is derived from that of the base. Thus we have the sulphat of potash, the sulphat of soda, &c. sulphur, phosphorus, and other bodies, it has already been observed, are susceptible of different degrees or stages of oxygenation; and afford, in these different stages, acids which are characterized by a peculiar train of properties. The compounds, also, which result from the union of two different acids, having the same combustible base, with alkalies and earths, are altogether different from each other. The salt, for example, which sulphuric acid affords with potash, is wholly unlike that which results from the combination of sulphurous acid with the same base. It was necessary, therefore, to distinguish the compounds of the more oxygenated from those of the less oxygenated acid; and this has been done by changing the termination from ate to ite. Thus the salts, formed with sulphurous and phosphorous acids, are called sulphites and phosphites; as sulphite of potash, phosphite of soda, &c.

An important law has been deduced, by Berzelius, respecting the combination of acids with bases, viz. that the quantities of different bases, required to saturate a given quantity of any acid, all contain the same quantity of oxygen. For example, 100 parts of sulphuric acid are saturated by a quantity of any base, containing 20 parts of oxygen; and 100 parts of muriatic acid by a quantity of base, which holds in combination 30.49 parts of oxygen. These proportions do not seem to be changed by varying the state of oxygenation in the acid; for sulphites absorb oxygen to become sulphates, and still remain neutral; the phosphites, when changed into phosphates, give up phosphorus, and continue neutral. It would appear, therefore, that the proportion between the oxygen of the acid, and that of the base, is regulated by the proportion of the combustible ingredients of the acid and base to each other. In sulphurets, for example, the metal and sulphur are in such proportion, that when both are oxygenated, the oxide, resulting from the one, precisely saturates the acid, resulting from the other. These facts strongly confirm the atomic theory, and cannot, indeed, be explained by any other.

Hitherto, we have considered the compounds of acids with their respective bases only in the state of neutral compounds, in which neither the acid, nor the base predominates. But we have several instances, in which a neutral compound is susceptible of uniting

with an additional quantity of acid or of base, and thus of acquiring an entirely new set of properties. Potash and tartaric acid, for example, when united in the proportions which neutralize each other, compose an extremely soluble salt, which has no action on vegetable colours; but with a double proportion of acid, a salt is formed, which requires a large quantity of water for solution, has an acid

taste, and instantly reddens vegetable blue colours.

To distinguish this and other other similar salts, the epithet acidulous was first proposed; but, for the sake of brevity, it has now become customary to prefix the Latin preposition super. Thus we have the super-tartrate of potash; the super-sulphate of potash; &c. On the contrary, when the base is predominant, we denote the deficiency of acid by the preposition sub, as sub-carbonate of potash, sub-borate of soda, &c. In the instance of the compounds of oxalic acid with potash, Dr. Wollaston has employed the words binoxalate and quadroxalate, to express the proportions in which the acid unites with the base; and this method of nomenclature he has extended to other salts, formed by the union of an acid and base in different proportions. There are several cases, however, in which it is extremely difficult to decide, whether a salt is to be classed among neutral, or among sub or super salts\*.

Thore are few instances of salts with compound bases; and in cases of this kind it is customary to annex to the generic name those of both the bases. Thus, for example, we have the tartrate of potash and soda, the phosphate of ammonia and magnesia, or as it is some-

times called, ammoniaco-magnesian phosphate.

In no part of chemistry is the advantage of the new nomenclature more sensibly experienced, than in the class of neutral salts; for the number of these compounds is susceptible of being multiplied to an immense extent. If the knowledge of the name did not lead to that of the compound, scarcely any memory would be adequate to retain them. But by changing the arbitrary titles, formerly assigned to them, for names expressive of their composition, we are furnished with a kind of artificial memory, which renders their recollection perfectly easy. Thus for the terms, butter of antimony, sugar of lead and Glauber's salt, are now substituted the more appropriate epithets of muriate of antimony, acetate of lead, and sulphate of soda.

Of those acids, which are supporters of combustion, a few retain the same property even in combination. Nitrate of potash, it is well known enters into active inflammation with charcoal, sulphur, and other combustible bodies. This is owing to the quantity of oxygen which the nitric acid contains, and which is less strongly attracted

by the nitrogen than by the newly added body.

Other properties, general to the class of salts, have already been described in the section on cohesion; especially their solubility, and their crystallization. On this last subject, it is necessary to add the general law deduced by Berzelius, viz. that in all salts, the water of crystallization contains a quantity of oxygen either equal to

<sup>\*</sup> See the remarks of Berzelius, Ann. de Chim. lxxix. 264, and lxxxii. 225.

that of the base; or a multiplication of it by 1, 2, 3, 4, &c. as far as 10; or a division by the same numbers. In sub-carbonate of soda, and muriate of ammonia, the quantity of oxygen in the water is equal to the oxygen in the base; in muriate of barytes, and in sulphates of ammonia and lime, the oxygen of the water is double that of the base; in green sulphate of iron, the oxygen of the water is seven times that of the oxide of iron; and, lastly, in carbonate and phosphate of soda, it is ten times that of the base.\*

The decrepitation of salts when suddenly heated, or expulsion of water from them with noise, is owing probably to the water being held not chemically but mechanically; for it is observed only in salts, which contain too small a quantity of water, to allow its being considered as an essential element; such as sulphate of potash, and

muriate of soda.

The deliquescence of salts has been observed by Gay Lussac to bear proportion to the temperature, at which saturated solutions of the respective salts boil. The more deliquescent the salt, the higher is the boiling point of its solution; and if not deliquescent at all, the boiling point of the solution is the same as that of watert.

Having premised these general observations respecting the acids and their compounds, I shall proceed to the history of the different acids, and of the compounds which they yield with the several alkaline and earthy bases. Under each head, I shall first enumerate the properties of the base of the acid; and its combinations with such other combustible bodies, as may already have been introduced to the reader's notice.

#### CHAPTER XI.

CARBONIC ACID AND ITS BASE.—CARBONATES.—BINARY COMPOUNDS OF CARBON.

THE bodies, which form the subject of this chapter, will be described in the following order:

I. Carbon, and its various modifications.

II. The compound of carbon and oxygen, in its highest state of oxygenation, constituting CARBONIC ACID; and, connected with it, the class of salts called CARBONATES.

III. The oxide of carbon, or carbonous oxide, a compound

containing less oxygen than exists in carbonic acid.

IV. The various combinations of carbon and hydrogen, termed CARBURETED HYDROGEN.

## SECTION I.

#### Carbon and Charcoal.

Ir had long been admitted as an established truth, chiefly on the evidence of the experiments of Guyton‡, that the diamond is the on\*80 Ann. de Chim. 187, note. †82 Ann. de Chim. 171. ‡Ann de Chim. xxxi.

ly form of pure carbon; and that charcoal is a compound of carbon and oxygen, or an oxide of carbon. The important experiments of Messrs. Allen and Pepys have suggested, however, that the diamond and charcoal, though so widely remote from each other in external characters, are, as to their chemical nature, identically the same; and that the difference between them, in all probability, results merely from the respective states of aggregation of their particles.

Some doubts, it must be confessed, were thrown on this conclusion by an experiment of Sir H. Davy, in which an inflammable gas was obtained, by igniting charcoal, in a Toricellian vacuum, by a powerful Voltaic battery. But the hydrogen, thus evolved, may reasonably be ascribed to water, from which it is extremely difficult to free charcoal. The absence of oxygen from charcoal was proved, by heating it with potassium, for no potash was produced; but when potassium was heated with diamond, there was an indistinct appearance of the production of that alkali. The recent experiments of the same philosopher\* tend to establish, that charcoal invariably contains either hydrogen or water; for when it is burned in pure and dry oxygen gas, some moisture is always deposited. The quantity, however, is so small, that hydrogen cannot exist in charcoal as an essential ingredient, or in any definite proportion. The diamond . appears to be absolutely free both from water and hydrogen; and itis in this respect only, and in the mechanical arrangement of its particles, that we have any evidence of its differing from charcoal. proof were wanted of the identity of the two substances, it is furnished by the fact that the diamond converts iron into steel, under circumstances quite free from all sources of fallacyt.

To obtain charcoal free from contamination, pieces of oak, willow, hazle, or other woods, deprived of the bark, may be buried in sand in a crucible, which is to be exposed, covered, to the strongest heat of a wind-furnace. For purposes of accuracy, charcoal must be used when recently prepared, and before it has had time to become cold; or if it cannot be had fresh made, it must be heated again

to redness, under sand in a crucible. The A remarkably pure charcoal may be obtained, by passing the vapour of oil of turpentine, or of spirit of wine, through a red-hot tube. It then appears in the form of a black impalpable powder. In the experiments of Sir H. Davy, this sort of charcoal, by combustion in oxygen gas, gave a much smaller product of moisture than any other.

From 100 parts of each of the following woods Messrs. Allen and Pepys obtained the annexed quantities of charcoal; viz. from fir, 18.17; lignum vitæ, 17.25; box, 20.25; beech, 15; oak, 17.40; mahogany, 15.75.

Charcoal has the following properties:

1. In its aggregated state it is black, perfectly insipid, and free from smell; insoluble in water, brittle, and easily pulverized. In close vessels, and entirely secured from contact with air, it is unchanged by any degree of heat. A gas, however, may be collected from it by distillation, which consists of hydrogen and carbon, and

<sup>\*</sup> Phil. Trans. 1814, p. 557.

<sup>†</sup> Phil. Trans. 1815. p. 371.

perhaps a little oxygen. Berthollet has found, also, in the aëriform products of its distillation, a considerable proportion of nitrogen\*.

2. Charcoal has the singular property of absorbing gases without alteration. Fill a jar with common air, or any other gas, and place it over dry mercury: take a piece of charcoal, red-hot from the fire, and plunge it in the mercury of the bath; when cold, let it be passed into the vessel of gas, without bringing it into contact with the atmosphere. A considerable diminution of the gas will be effected; and in 24 or 36 hours will be completed.

Count Morozzo has given the following table of the quantity of different gases absorbed, in the foregoing manner, by charcoal. In each experiment, he employed a piece of that substance 1 inch long and 3 of an inch diameter. The receiver containing gas was 12

inches long and 1 inch diameter.

Gas absorbed. Inch	es.   Gas aborbed.	Inches.
Atmospheric	Si Nitrous	65
Carbonic acid ! 1	1 Hydrogen	$2_{12}$
Ammonia 1	1 Oxygen	$2\frac{1}{4}$
Muriatic acid 1	1   Sulphurous acid	
Sulphureted hydrogen 1	1	•

This property of charcoal has been made the subject of a valuable set of experiments by Saussuret. Charcoal of boxwood he found to absorb, of

	olumes.
Ammoniacal gas	90
Muriatic acid	85
Sulphurous acid	65
Sulphureted hydrogen	55
Nitrous oxide	40
Carbonic acid	<b>35</b> .
Olefiant gas	35
Carbonic oxide	9.42
Oxygen	9.25
Azote	7.5
Hydrogen	1.75

Most of the phenomena attending this absorption have already been described, in speaking (chap. v. sect. i.) of the absorption of gases by solids. It appears to be entirely a mechanical effect; for even those gases that have an affinity for charcoal (hydrogen and oxygen for instance), are given out unchanged at the heat of boiling water. The densest and heaviest kinds of charcoal are most remarkable for this property, which is much diminished by pulverizing them; and does not exist at all in plumbago or in stone coal.

8. From the experiment of Rouppe\*, it appears, that if charcoal, which has imbibed oxygen gas, be brought into contact with hydrogen gas, water is generated; but Saussure, by a careful repetition of it, could not obtain the same result.

<sup>\*</sup> Memoires d'Arcueil, ii. 484.

<sup>‡</sup> Ann. de Chim. xxxii. 1.

<sup>†</sup> Thomson's Annals, vi. 241,

4, Charcoal, by long exposure to the atmosphere, absorbs one

twentieth of its weight, three fourths of which are water\*.

The charcoal of different woods, Messrs. Allen and Pepys found to increase very differently in weight; that from fir, gaining, by a week's exposure, 13 per cent.; that from lignum vitæ, in the same time, 9.6; from box 14; beech, 16.3; oak, 10.5; mahogany, 18. The absorption goes on most rapidly during the first 24 hours; and by much the largest part of what is absorbed consists of water merely.

5. Charcoal resists the putrefaction of animal substances. A piece of flesh-meat, which has begun to be tainted, may have its sweetness restored by rubbing it daily with powdered charcoal; and may be preserved sweet for some time by burying it in powdered charcoal, which is to be renewed daily. Putrid water is also restored by the application of the same substance; and water way be kept unchanged at sea, by charging the inner surface of the casks which are used to contain itt. It produces, also, a remarkable effect in destroying the taste, odour, and colour of many vegetable and animal substances. Common vinegar, by being boiled on it, is rendered perfectly limpid. Rum and other varieties of ardent spirit, which are distinguished by peculiar colours and flavours, lose both by maceration with powdered charcoal. The colour of litmus, indigo, and other pigments, dissolved or suspended in water, is destroyed. Putrid animal fluids, and air contaminated with offensive fumes, are, also, completely deprived of their odour. These effects are most readily produced by animal charcoalt.

6. Charcoal is a very slow conductor of caloric. The experiments of Guyton have been determined, that caloric is conveyed through charcoal more slowly than through sand, in the proportion of three to two. Hence powdered charcoal may be advantageously employed to surround substances which are to be kept cool in a warm atmos-

phere: and also confine the caloric of heated bodies.

7. The weight of the atom of charcoal is inferred by Mr. Dalton to be 5.4, that of oxygen being 7. But if the weight of the atom of oxygen be corrected to 7.5, the atom of charcoal will then weigh 5.8. The evidence in favour of this conclusion will be stated in the following section. The specific gravity, which it would have, if reducible into a vaporous form, is calculated by Gay Lussac to be 0.416.

## SECTION II.

# Combustion of Carbon.

If a small piece of charcoal be exposed red-hot to the common atmospheric air, it exhibits scarcely any signs of combustion, and soon becomes cold. Sir H. Davy has indeed lately observed that dry

<sup>†</sup> Clement and Desorms. † Lovitz, Ann. de Chim. tom. xiv. ‡ 79 Ann. de Chim. 80; Journ. of Science, &c. iv. 367.

charcoal converts oxygen gas pretty rapidly, though imperceptibly, into carbonic acid, if kept at a temperature a little above the boiling point of quick-ilver\*. And if a piece of charcoal, heated to about 800° or 1000° Fahrenheit, or nearly to redness, be introduced into a receiver filled with oxygen gas, it continues to burn with greatly increased splendour, and with bright scintillations. If the charcoal be pure, and its proportion rightly adjusted, it is entirely consumed. When the quantity burnt is considerable, a manifest production of water takes place, and the inner surface of the glass vessel becomes covered with moisture, which disappears, however, on standing. This portion of water owes its origin to the union of oxygen with the hydrogen, which, it appears from Sir H. Davy's experiments, and from the

results of its distillation, all charcoal contains.

The diamond, also, which was formerly considered as an incombustible substance, may be consumed by a sufficiently intense heat, even in atmospherical air. The Florentine academicians, in the year 1694, appear first to have ascertained this fact, by exposing diamonds to the focus of a powerful burning lens. Their experiment has been repeated by subsequent chemists, with various modifications. It has been found by Sir George Mackenzie that diamonds burn when exposed on a muffle, to the temperature of about 14° Wedg-In oxygen gas the diamond takes fire, when the focus of a powerful lens is thrown upon it; and continues to burn, though removed out of the focus, with a steady brilliant light, visible in the strongest sunshinet. The portion of diamond, which remains unconsumed, is not rendered black, as has been asserted, but is found to have lost its lustre, like glass acted on by fluoric acid. When the vessel has become cold, no production whatsoever of mois-By effecting its combustion in this way, Guyton ture is visible. thought he had determined that the diamond, in an equal weight, contains more real carbon than exists in common charcoal. His experiments, however, have not been confirmed by those of subsequent One fact, however, has been contributed on this subject by Guyton, which is of considerable value. The diamond, he first ascertained, is destroyed when thrown into red-hot and melted nitre; and this property, it will afterwards appear, has been succesfully applied by Mr. Tennant to the determination of the nature of the diamond, and of the proportion of ingredients in carbonic acid.

To collect the products of the combustion of carbon, requires rather a complicated apparatus. Lavoisier burnt charcoal in a known quantity of oxygen gas, which was confined by mercury, the charcoal being set on fire by a bent iron wire heated to redness. Messrs. Allen and Pepys collected the products of the combustion of charcoal and of the diamond, by burning them separately in a platinum tube, set horizontally in a charcoal furnace, and connected, at each extremity, with a mercurial gazometer. An idea of this arrangement will best be obtained by imagining that to each

<sup>\*</sup> Phil. Trans. 1817, p. 16. † Davy, in Phil. Trans. 1814. † Elements of Chemistry, pl. iv. fig. 3.

end of the tube c, fig. 40, the pipe b of a gazometer, like that shown fig. 35, is connected. At the outset of the experiment, one of the gazometers was filled with a known quantity of the purest oxygen gas, and the other was empty. The tube was then made red-hot; and the gas, being forced alternately from one gazometer to the other, was repeatedly brought into contact with the red-hot charcoal or diamond. The volume of the gas was found to be entirely unaltered; but it had received an addition to its weight, precisely equal to what the charcoal or diamond, on weighing, was ascertained to have lost; and it was partly converted into a gas, totally different in its properties from oxygen gas, and called carbonic It appears, therefore, that oxygen gas, by conversion into acid. carbonic acid, undergoes neither expansion nor condensation. This conclusion is farther established by the recent experiments of Sir H. Davy, on the combustion of the diamond in oxygen gas.

## SECTION III.

#### Carbonic Acid.

From the quantity of charcoal or diamond consumed in the experiments of Allen and Pepys, and the quantity of oxygen converted into carbonic acid, it is easy to infer the proportion of carbon and oxygen in the new compound. Reducing these to centesimal proportion, for every 28 or 29 grains of the combustible base which disappeared, 100 grains of carbonic acid (= about 201 cubic inches) were generated; and it is remarkable that these proportions agree exactly with those originally stated by Lavoisier. The same quantity of carbonic acid resulted, also, from the combustion of between 28 and 29 grains of diamond. Hence it may be inferred, that the actual quantity of carbon in equal weights of diamond and charcoal is precisely the same; and the charcoal is not, as has hitherto been supposed, an oxide of carbon. If this inference required confirmation, it is furnished by its agreement with Mr. Tennant's experiments on the combustion of the diamond, published in 1797. Two grains and a half of diamond (this philosopher found), when consumed in a tube of gold by means of nitre, gave nine grains of carbonic acid, which, in 100 parts should contain, therefore, as nearly as possible, 28 parts of diamond or carbon. The mean of a number of Messrs. Pepys and Allen's experiments give the following statement of the composition of carbonic acid:

Carbon . . . , . . . . 28 60 . . . . . . . 100 Oxygen . . . . . . . 71.40 . . . . . . . 250

100.

It is remarkable, also, that these numbers are precisely those, which result from the experiments of Clement and Desormes\*.

\* Ann. de Chim. xxxix. 42.

They differ, however, a little, from those of Saussure, jun., who states the carbon in 100 grains of carbonic acid at between 27.04 and 27.38 grains. The results of Gay Lussac, which are conformable with the views of Berzelius, and, as nearly as possible, with those of Dr. Wollaston, are,

					100 265.12		. 37.55 . 100.
•		100.	•		355.12		137.56
		100.			333.12		137.30

Mr. Dalton assumes the composition of carbonic acid to be, in round numbers, 28 of charcoal and 72 of oxygen; from whence he deduces the weight of the atom of charcoal to be 5.4. But if the atom of oxygen weigh 7.5, and if the proportions of Gay Lussac be correct, the atom of charcoal will weigh 5.65, and that of carbonic acid (considering it as a ternary compound of two atoms of oxygen and one of charcoal) will be 20.65.

In addition to the proofs of the constitution of carbonic acid, derived from its synthesis, we have also the evidence of its analysis,

which may be effected by several processes.

1. By passing a succession of electrical discharges through a quantity of carbonic acid gas confined over mercury, I have found that the gas is separated into oxygen, and a gas called carbonous oxide, which consists of oxygen united with a larger proportion of carbon, than exists in carbonic acid. When the carbonic acid, which escapes decomposition, is washed out by solution of potash, an electric spark inflames the residuary mixture; the oxygen and carbonous oxide again uniting, and re-composing carbonic acid\*.

2. When a mixture of carbonic acid and hydrogen gases is electrified, the hydrogen combines with part of the oxygen in the acid,

and reduces it to the state of carbonous oxide.

3. When potassium is heated in carbonic acid gas, Sir H. Davy has found that it inflames; part of it is oxidated at the expense of the acid; and part of it unites with the charcoal, which is precipitated.

4. By simply heating phosphorus in carbonic acid gas, no step is made towards the decomposition of the latter. But by applying phosphorus to some of the combinations of carbonic acid, the phosphorus is oxygenated, and carbon appears in a separate form. The original discovery of this fact is due to Mr. Tennant, and the details of the experiment have been ably followed up by Dr. Pearson.

To exhibit this fact, provide a tube of very thin glass, about one third of an inch wide, and 18 or 20 inches long, sealed at one end. Coat it, within about an inch of the sealed extremity, with a lute of sand and clay; and when this is dry, put into it as much purified phosphorus, in small pieces, as will fill the uncoated part. Then cover the phosphorus with carbonate of lime, or carbonate of soda which

<sup>\*</sup> Phil. Trans. 1809. p. 448. ‡ Ibid 1792, p 289.

has been deprived of its water of crystallization. Let the part of the tube, which contains the carbonate, be made red-hot by means of a portable furnace; and, at this moment, apply heat to the part containing the phosphorus, sufficient to melt and raise it into vapour. The vapour of the phosphorus, coming into contact with the red-hot carbonate, will decompose the carbonic acid; and charcoal will be found in the residue of the process, in the form of a very light and

black powder.

To procure carbonic acid, sufficiently pure for the exhibition of its properties, the combustion of charcoal is far from being the best process. The student may, therefore, have recourse to another, the rationale of which he will not, at present, understand; but which, will be explained afterwards. Into a common gas bottle, put a little powdered marble or chalk, and pour on this, sulphuric acid, diluted with five or six times its weight of water. A gas will be produced, which those, who have an opportunity, may receive over mercury; but a mercurial apparatus is not absolutely essential, since the gas may be collected over water, if used immediately when procured. Carbonic acid may, also, be separated by heat alone, from carbonate of lime. For this purpose, coarsely powdered chalk or marble may be put into the iron vessel  $\alpha$ , fig. 85, which may be connected, by means of the conducting pipe b, with a gazometer. The receiving cylinder of the latter, after a sufficiently long continuance of heat to the bottle a, will be filled with carbonic acid gas. Its properties are the following:

# Properties of Carbonic Acid.

(a) It extinguishes flame.—Set a vessel, filled with the gas, with its mouth upwards, and let down a lighted candle. The candle will

instantly be extinguished.

A person, says Dr. Priestley, who is quite a stranger to the properties of this kind of gas, will be agreeably amused with extinguishing lighted candles, or blazing chips of wood, on its surface. For the smoke readily unites with this kind of air; so that little or none of it escapes into the atmosphere. It is remarkable, that the upper surface of this smoke, floating in the fixed air, is smooth and well defined; whereas the lower surface is exceedingly ragged, several parts hanging down to a considerable distance within the body of the carbonic acid, and sometimes in the form of balls, connected to the upper stratum by slender threads, as if they were suspended. The smoke is also apt to form itself into broad flakes, exactly like clouds. Making an agitation in this air, the surface of it (which still continues exactly defined) is thrown into the form of waves; and if, by this agitation, any of the carbonic acid be thrown over the sides of the vessel. the smoke, which is mixed with it, will fall to the ground, as if it were so much water.

(b) It is fatal to animals.—Put a mouse, or other small animal, into a vessel of the gas, and cover the vessel, to prevent the contact of common air. The animal will die in the course of a minute or two.

By means of this gas, butterflies, and other insects, the colours of which it is desirable to preserve, for the purpose of cabinet specimens, may be suffocated better than by the common mode of killing them

with the fumes of sulphur.

(c) This gas is heavier than common air.—According to Sir H. Davy, 100 cubic inches, at 55° Fahrenheit, and 30 inches of the barometer, weigh 47.5 grains; and at 60°, with the same pressure, would weigh 47.11. Messrs Allen and Pepys have lately determined that 100 cubic inches, at 60° Fahrenheit, and 30 inches barometer, weigh 47.26 grains. Its specific gravity, according to Biot and Arajo, is 1.5196; and hence, if 100 cubic inches of atmospheric air weigh 30.5 grains, the same bulk of carbonic acid gas should weigh 46.34 grains; Dr. Ure finds it to be 46.4. It will be a sufficiently near approximation to state the weight of 100 cubical inches to be 47

grains, at a mean of the barometer and thermometer.

To show the superior specific of gravity of this gas in a general way, the following experiment will be sufficient. Let a long glass tube, proceeding from a gas bottle, containing powdered marble and dilute sulphuric acid, be twice bent at right angles; let the open end of the longer leg reach the bottom of a glass jar, perfectly dry within, and standing with its mouth uppermost. The carbonic acid will expel the common air from the jar, because it is heavier.—This superior gravity may be farther shown as follows: When the jar is perfectly filled with the gas (which may be known by a lighted candle being instantly extinguished when let down into it), take another jar, of rather smaller size, and place at the bottom of it a lighted taper, supported by a stand: then pour the contents of the first-mentioned jar into the second, as if you were pouring in water. The candle will be instantly extinguished, as effectually as if it had been immersed in water.

It is owing to its superior gravity, that carbonic acid gas is often found at the bottom of deep wells and of mines, the upper part of which is entirely free from it. Hence the precaution, used by the sinkers of wells, of letting down a candle before they venture to de-

scend in person.

(d) Carbonic acid gas is absorbed by water.—Fill partly a jar with this gas, and let it stand a few hours over water. An absorption will gradually go on, till at last none will remain. This absorption is infinitely quicker when agitation is used. Repeat the above experiment, with this difference, that the jar must be shaken strongly. A very rapid diminution will now take place. In this manner water may be charged with rather more than its own bulk of carbonic acid gas; and it acquires, when thus saturated, a very brisk and pleasant taste. This impregnation is most commodiously effected by an apparatus, sold in the glass shops, under the name of Nooth's machine.

The influence of pressure, in occasioning water to absorb a large quantity of carbonic acid, may be illustrated by an apparatus, which I have described in the Philosophical Transactions for 1803, but which cannot be understood without the engraving that accompanies it. From a long series of experiments with this apparatus, I have

deduced, as a general law, that water takes up the same volume of compressed carbonic acid gas, as of gas under ordinary pressure. And since the space occupied by any gas, is inversely as the compressing force, it follows that the quantity of gas, forced into water, is directly as the pressure. Thus, if water under common circumstances takes up an equal bulk of carbonic acid, under the pressure of two atmospheres, it will absorb twice its bulk; under three atmospheres three times its bulk, and so on.

(e) From water, thus impregnated, carbonic acid is again set at liberty, on boiling the water, or by exposing it under the receiver of an air-pump.—During exhaustion, the gas will escape so rapidly, as to present the appearance of ebullition; and will be much more remarkable than the discharge of air from a jar full of common spring water, confined, at the same time, under the receiver, as a standard

of comparison.

(f) Carbonic acid is expelled from water by freezing.—If the impregnated water be rapidly congealed, by surrounding it with a mixture of snow and salt, the frozen water has more the appearance of snow than of ice, its bulk being prodigiously increased by the immense number of air bubbles. When water, thus congealed, is liquefied again, it is found, by its taste, and other properties, to have lost

nearly the whole of its carbonic acid.

(g) Carbonic acid gas, when combined with water, reddens vegetable blue colours.—This may be shown by dipping into water, thus impregnated, a bit of litmus paper, or by mixing, with a portion of it, about an equal bulk of the infusion of litmus. This fact establishes the title of the gas to be ranked among acids. When an infusion of litmus, which has been thus reddened, is either heated, or exposed to the air, its blue colour is restored, in consequence of the escape of the carbonic acid. This is a marked ground of distinction from most other acids, the effect of which is permanent, even after boiling.

(h) Carbonic acid gas precipitates lime water.—This character of the gas is necessary to be known, because it affords a ready test of the presence of carbonic acid whenever it is suspected. Pass the gas, as it proceeds from the materials, through a portion of lime water. This, though perfectly transparent before, will instantly grow milky: Or, mix equal measures of water saturated with carbonic acid and lime water. The same precipitation will ensue. By means of lime water, the whole of any quantity of carbonic acid, existing in a mixture of gases, cannot, however, be removed, as Saussure jun. has shown; but recourse must be had, in order to effect its entire absorption, to a solution of caustic potash or soda.

(i) By the application of the test (h) it will be found, that carbonic acid is generated in several cases of combustion,—1. Let the chimney of a small portable furnace, in which charcoal is burning, terminate, at a distance sufficiently remote to allow of its being kept cool, in the bottom of a barrel provided with a moveable top, or of a large glass vessel having two openings. A small jar of lime water being let down into the tub or vessel, and agitated, the lime water will immediately become milky. The gas will also extinguish burn-

ing bodies, and prove fatal to animals that are confined in it. Hence the danger of exposure to the fumes of charcoal, which, in several instances, have been known to be fatal. These fumes consist of a mixture of carbonic acid and nitrogen gases with a very small proportion of oxygen gas. 2. Fill the pneumato-chemical trough with lime water, and burn a candle, in a jar filled with atmospheric air, over the lime water till the flame is extinguished. On agitating the jar, the lime water will become milky. The same appearances will take place, more speedily and remarkably, if oxygen gas be substituted for common air. The carbonic acid, thus formed during combustion, by its admixture with the residuary air, renders it more unfit for supporting flame, than it otherwise would be from the mere loss of oxygen. Hence, if a candle be burnt in oxygen gas, it is extinguished long before the oxygen is totally absorbed, because the admixture of carbonic acid with oxygen gas, in considerable proportion, unfits it for supporting combustion. Whenever any substance, by combustion in oxygen gas or common air over lime water, gives a precipitate, soluble with effervescence in muriatic acid, we may confidently infer that it contains carbon.

(k) The respiration of animals is another source of carbonic acid.—On confining an animal in a given portion of atmospheric air, over lime water, this production of carbonic acid is evinced by a precipitation. The same effect is also produced more remarkably in oxygen gas. The production of carbonic acid, by respiration, may be proved, also, by blowing the air from the lungs, with the aid of a quill, through lime water, which will immediately grow milky. The carbonic acid, thus added to the air, unfits it for supporting life, not merely by diminishing the proportion of oxygen gas, but apparently by exerting a positively noxious effect. Hence a given quantity of air will support an animal much longer, when the carbonic acid is removed as fast as it is formed, than when suffered to remain in a state of mixture. It has been found, that an atmosphere, consisting of oxygen gas and carbonic acid, is fatal to animals, though it should contain a larger proportion than the air we commonly breathe.

(1) Carbonic acid is at all times present in the air of the atmosphere.—This might naturally be expected from the immense quantity which is constantly produced by respiration and combustion. Its presence is demonstrated by leaving a shallow vessel of lime water exposed to the atmosphere; for its surface is soon covered with a solid pellicle, which, when removed, is succeeded by another, and so on, till the water is deprived of all the lime, which it held in solution. From the precipitate, thus formed, carbonic acid is disengaged by dilute acids.

The quantity of carbonic acid, present in atmospheric air, is estimated by Mr. Dalton not to exceed one thousandth of its bulk. Saussure examined its proportion in the air of an open field, a few miles from Geneva\*. In January, the mean of three experiments showed 4.79 parts in 10,000; in July and August, 7.18 parts in the

<sup>\*</sup> Ann. de Chim. et Phys. ii. 199; and iii. 170.

same volume, which is even considerably short of the small proportion determined by Mr. Dalton. The difference between the quantities discovered in summer and winter, though on first view very small, viz. 2,30 volumes in ten thousand, would constitute so large a quantity, when the whole atmosphere is taken into the account, that the fact can scarcely be considered as determined without repeated and careful experiments.

(m) Carbonic acid retards the putrefaction of animal substances.

This may be proved, by suspending two equal pieces of flesh meat, the one in common air, the other in carbonic acid gas, or in a small vessel through which a stream of carbonic acid is constantly passing. The latter will be preserved untainted some time after the other has

begun to putrefy.

(n) Carbonic acid gas exerts powerful effects on living vegetables.—These effects, however, vary according to the mode of its

application.

Water, saturated with this gas, proves highly nutritive, when applied to the roots of plants. The carbonic acid is decomposed, its carbon forming a component part of the vegetable, and its oxygen

being liberated in a gaseous form.

On the contrary, carbonic acid, when a living vegetable is confined in the undiluted gas over water, is injurious to the health of the plant, especially in the shade. The late Mr. Henry, long ago found that a certain quantity of fixed air, applied as an atmosphere, is favourable to vegetation; and M. Saussure, of Geneva, has determined more recently, that the mixture of more than i of carbonic acid with common air is always injurious; but that in this proportion it promotes the growth of plants, and is manifestly decomposed.

Carbonic acid is susceptible of combination with alkalies, earths, and metals, and forms an order of compounds, termed carbonates. At present, however, we shall only attend to the results of its union with alkalies, and earths. In the compounds of carbonic acids with these bases, and especially with the alkalies, the qualities of the base still predominate. The alkaline carbonates, for example, retain the taste, though in a less degree, which characterizes their bases; and change blue vegetable colours to green. Ammonia, also, preserves in a great measure its odour and volatility. By combination with the earths, however, carbonic acid produces a more perfect neutralization of their properties.

#### SECTION IV.

#### Carbonates.

# ART. I .- Sub-carbonate, and Bi-carbonate of Potash.

(a) Carbonic acid gas is very abundantly absorbed by a solution of pure potash.—The simplest mode of showing this fact is the fol-

lowing: Fill a common phial with carbonic acid gas over water; and when full, step it by applying the thumb. Then invert the bottle in a solution of pure potash, contained in a cup, and rather exceeding in quantity what is sufficient to fill the bottle. The solution will rise into the bottle, and, if the gas be pure, will fill it entirely. Pour out the alkaline liquor, fill the bottle with water, and again displace it by the gas. Proceed as before, and repeat the process several times. It will be found, that the solution will condense many times its bulk of the gas; whereas water combines only with its own volume.

This experiment may be made, in a much more striking manner, over mercury, by passing into a jar, about three fourths filled with this gas, a comparatively small bulk of a solution of pure potash which will condense the whole of the gas. If drylpotash be substituted in this experiment, no change will ensue; which proves, that solution is essential to the action of alkalies on this gas.

One hundred grains of potash unite with 42.42 carbonic acid to form the sub-carbonate, which, therefore, contains per cent. accord-

ing to Berard.

Potash . . . . . 70.21 Acid . . . . . . 29.79

100.

The composition of this salt is differently stated by other writers, viz.

		Acid. Base.
According to Dalton 100 grains consist	of	31.10 68.9
Dulong		
Dr. Wollaston		31.71 68.29
Vauquelin :		33 67.*

The proportions of 70 to 30 agree very nearly with the notion, that the sub-carbonate of potash is constituted of an atom of carbonic acid, weighing 20.8, and an atom of potash weighing 50; and that the weight of its atom is 70.8. The affinity of carbonic acid for potash, though apparently feeble, is in reality very strong; since it has the power of expelling, from potash, the whole of the water,

which that alkali contains in the state of a hydrate.

(b) The changes effected in the alkali may next be examined.—It will be found, after having absorbed as much carbonic acid as it is capable of condensing, to have lost much of its corrosive and penetrating taste, and will no longer destroy the texture of woollen cloth; but it still turns to green the blue infusion of vegetables. Before its absorption of this gas, no remarkable change ensued on mixing it with diluted sulphuric acid; but if this, or almost any other acid, be now added, a violent effervescence will ensue, arising from the escape of the gas that had been previously absorbed. If the mixture he made in a gas bottle, the gas, that is evolved, may be collected, and will be found to exhibit every character of carbonic acid.

For experimental purposes, sub-carbonate of potash may be ob-

tained from crystals of tartar (super-tartrate of potash) calcined in a crucible; then lixiviated with water; and evaporated to dryness. By this treatment, the salt yields aboutone third its weight of subcarbonate. Or it may be mixed with about an eighth of purified nitrate of potash, and wrapped up in paper in the form of cones, which may be placed on an iron dish, and set on fire. The residuary mass is to be lixiviated, and evaporated as before directed. Or purified nitrate of potash may be mixed with a fourth of its weight of powdered charcoal, and projected into a red-hot crucible, the contents of which are to be poured, when in fusion, into an iron dish. The sub-carbonate, thus obtained, amounts to rather less than one half the nitre which has been employed. Even when thus prepared, it is apt to contain some impurities, consisting chiefly of a minute proportion of sulphate and muriate of potash, with a little silex, from which it is extremely difficult entirely to free it. That which is procured from burnt tartar may be made to crystallize, in which state it contains 20.60 per cent. of water.

(c) In this state of sub-saturation with carbonic acid, potash generally occurs in the arts. The potash and pearlash of commerce, are sub-carbonates of potash, of different degrees of purity. The quantity of carbonic acid, contained in these alkalies, may be learned by a very simple experiment. Put one or two hundred grains of the alkali into a Florence flask, and add a few ounce-measures of water. Take also a phial filled with dilute sulphuric acid, and place this, as well as the flask, in one scale. Balance the two, by putting weights into the opposite scale, and, when the equilibrium is attained, pour gradually the acid into the flask of alkali, till an effervesence no longer ensues. When this has ceased, the scale containing the weights will be found to preponderate. This shows that the alkali, by combination with an acid, loses considerably of its weight; and the exact amount of the loss may be ascertained, by adding weights to the scale containing the flask and phial, till the

balance is restored.

(d) As it is sometimes of importance to know what proportion of real alkali a given weight of potash or pearlash contains, it may be proper to point out how this information may be acquired. I shall, therefore, in Part III. Chap. III. of this work, describe at length

the apparatus and process best adapted to this purpose.

(e) Sub-carbonate of potash dissolves very readily in water, which at the ordinary temperatare, takes up more than its own weight.—Hence, when an alkali, which should consist almost entirely of subcarbonate of potash, is adulterated, as very often happens, with substances of little solubility, the fraud may be detected by trying how much of one ounce will dissolve in two or three ounce-measures of water. In this way I have detected an adulteration of one third its weight of sulphate of potash. There are certain substances of ready solubility, however, which may be used in adulterating pearlashes, as common salt for example; and, when this is done, we must have recourse to the acid test for the means of discovery.

The strongest solution of this salt that can be obtained has the

Vol. I.-H h

specific gravity 1.54, and contains 48.8 per cent. by weight, or eight atoms of water to one of salt.

(f) Sub-carbonate of potash, when exposed to the atmosphere, attracts so much moisture, as to pass rapidly to a liquid state. This change is termed *deliquescence*. All the water thus absorbed is expelled again by a heat of 280°.

(g) When submitted, in a crucible, to a high temperature, it fuses;

but none of its carbonic acid is expelled.

# Bi-carbonate of Potash.

Carbonate of potash, in the state which has been already described, is far from being completely saturated with acid. This sufficiently appears from its strongly alkaline taste. It may be much more highly charged with carbonic acid, by exposing a solution of one part of the sub-carbonate in three of water to streams of carbonic acid gas, in a Nooth's machine, or other apparatus; or by the process to be described in art. 3, g. When a solution of alkali, after this treatment, is very slowly evaporated, it forms regular crystals. According to Dr. Wollaston\*, the quantity of acid in the bi-carbonate is exacty double that in the sub-carbonate. This he proves by disengaging the carbonic acid from each, by a stronger acid, such as the sulphuric. One part of the bi-carbonate, thus treated, is found to give twice as much carbonic acid as the subsalt. Berthollett obtained 189 grains of carbonic acid from 500 of this salt; and as nearly as possible, the same quantity from 1000 grains of the salt, reduced by calcination to sub-carbonate. Berard found, that 100 parts of potash are fully saturated by 85.86 carbonic acid;. The following Table exhibits the composition of the bi-carbonate, as stated by him, and by Dr. Wollaston. One hundred grains contain

		Acid.	Base.	Water,
According to Berard		42.01	48.92	9.07
Dr. Wollaston				9.0
Vauquelin .		47.	46.	7.

The atomic constitution, deducible from these proportions, is one atom of potash, two atoms of carbonic acid, and one atom of water.

The bi-carbonate of potash differs from the sub-carbonate in

the following particulars.

1. In the greater mildness of its taste. Though still alkaline, yet it may be applied to the tongue, or taken into the stomach, without exciting any of that burning sensation, which is occasioned by the sub-carbonate.

2. It is unchanged by exposure to the atmosphere.

3. It assumes the shape of regular crystals. The form of these crystals is a four-sided prism, with dihedral triangular summits, the facets of which correspond with the solid angles of the prism.

Philosophical Transactions, 1808.
 † Mem. d'Arcueil, ii. 470.
 † 71 Ann. de Chim. 49.

4. It requires, for solution, four times its weight of water at 60°: and, while dissolving, absorbs caloric. Boiling water dissolves fivesixths of its weight; but, during this solution, the salt is partly decomposed, as is manifested by the escape of carbonic acid gas. The quantity thus separated amounts, according to Berthollet, to about th the weight of salt.

5. By calcination in a low red heat, the portion of carbonic acid, which imparts to this salt its characteristic properties, and water, are expelled, and the salt returns to the state of a sub-car-

bonate.

(k) Bi-carbonate of potash, in all its forms, is decomposed by the stronger acids; as the sulphuric, nitric, and muriatic, which unite

with the alkali, and set the gas at liberty.

This may be shown by pouring, on the carbonate contained in a gas bottle, any of the acids, and collecting the gas by a proper apparatus.

# ART. 2.—Carbonate of Soda.

There are two distinct compounds of carbonic acid and soda, the one containing precisely half as much carbonic acid as the other.

The first, or sub-carbonate, is obtained by carefully re-crystallizing the soda of commerce. The primitive crystal of this salt is an octohedron, with a rhombic base of 60° and 120°, the planes of which meet, at the summit, at 104°, and, at the base, at 76°. This crystal varies by becoming cuneiform, and also by the replacement of the solid angle of the summits by planes parallel to the base, affording the decahedral variety, which is most common. These crystals have the following properties.

1. When heated to 150° Fahrenheit, they fuse; boil violently, if the heat be raised; and leave a dry white powder. What escapes is water only; and it forms, according to Berard, 62,69 per cent. of the weight of the salt; to Kirwan, 64; Dalton, 63; and D'Arcet, 63.6. The crystals, also, lese their water by exposure to the atmos-

phere, or effloresce.

2. If the fused salt be kept boiling in a retort, Mr. Dalton finds that it deposits a hard, small-grained salt, which contains only 46 per cent. of water; the clear liquid has the specific gravity of 1.35; and, on cooling, concretes into a fragile icy mass. The first compound, Mr. Dalton estimates to consist of 1 atom of carbonate and 10 of water; the second of 1 atom of salt and 5 of water; and the third of 1 atom of salt and 15 of water.

3. Water at 60° takes up half its weight of the sub-carbonate; and boiling water dissolves rather more than its own weight. strongest solution, that can be preserved at the temperature of the atmosphere, has the specific gravity 1.26; but even this is liable to

partial crystallization.

4. If 100 grains of the salt be slowly added to a quantity of diluted sulphuric acid, more than sufficient for neutralization, and of known weight, the loss of weight will show the quantity of carbonic

acid contained in 100 grains. From experiments of this kind, joined with others on its loss by fusion, Berard deduces its composition to be

Acid .	•	13.98		•	•	100	•		•	60
Base . Water			•	•	•	166	•	•	•	100
,		100.								

Independently of the water of crystallization, its composition has been differently stated, viz. 100 grains contain

		Acid.		Base.
According to Berard .		\$7.50		62.50
Dulong .		40.09		59.91
Dalton .		40.40		,59 <b>.</b> 60
Klaproth				
Kirwan .		40.10		59.90

Its atomic constitution is supposed by Mr. Dalton to be one atom of soda with one atom of carbonic acid.

When a solution of the sub-carbonate of soda is saturated, by passing through it a stream of carbonic acid gas, or when a solution of 100 parts of the salt are heated with one of 14 parts of sub-carbonate of ammonia, we obtain by evaporation an indistinctly crystallized salt, which is the bi-carbonate of soda. The taste of this salt is much milder than that of the sub-carbonate; and it requires a much larger quantity of water for solution. To bring soda to this state of saturation, 100 parts of the alkali require 125.33 of carbonic acid. The bi-carbonate is, therefore, composed, in 100 parts.

	Acid.			Base.		Water.
According to Berard	, of 49.95	•	•	29.85		20.20
Rose						

And as the acid in this salt is, as nearly as possible, double that of the sub-carbonate, it must be constituted of two atoms of acid and one atom of soda. By exposure to a red heat, the whole of its water, and half of its carbonic acid, are expelled, and it is converted into the dry sub-carbonate.

# ART. 3.—Sub-carbonate and Bi-carbonate of Ammonia.

Ammonia, in its pure state, exists in the form of a gas, permanent over mercury only: and carbonic acid has, also, the form of an aërial fluid. But when these two gases are mixed together over mercury in proper proportions (viz. one measure of carbonic acid to two or three of alkaline gas), they both quit the state of gas, and are entirely condensed into a white solid body. The compound thus formed, it appears from the recent experiments of Gay Lussac, is the

sub-carbonate of ammonia; for the two gases, he finds, cannot by simple mixture, be made to unite in the proportions necessary to neutralize each other. To effect this, it is necessary to expose a solution of sub-carbonate of ammonia in water to carbonic acid gas, in which case the affinity of the water concurs in overcoming the

elasticity of the acid gas.

(a) Those persons who are not possessed of a mercurial trough may compose the sub-carbonate of ammonia in the following manner:—Provide a globular receiver, having two open necks opposite each other. Into one of these introduce the neck of a retort, containing carbonate of lime and dilute sulphuric acid, from which a constant stream of carbonic acid will issue. The inner surface of the globe will remain perfectly unclouded. Into the opposite opening, let the mouth of a retort be introduced, containing the materials for ammoniacal gas. (Chap. vii. sect. 2.) The inner surface of the globe will now be covered with a dense crust of carbonate of ammonia.

The sub-carbonate of ammonia may also be formed, by passing, into a jar three fourths filled with carbonic acid over mercury, a solution of pure ammonia, which will instantly effect an absorption of the gas. The ordinary mode of producing it for useful purposes will

be described hereafter.

(b) Sub-carbonate of ammonia retains, in a considerable degree, the pungent smell of the pure volatile alkali. It is, also, unlike the other sub-carbonates, volatilized by a very moderate heat, and evaporates without entering previously into a liquid state. The vapour that arises may be again condensed in a solid state; affording an example of sublimation. This may be shown, by applying heat to the sub-carbonate of ammonia in a retort, to which a receiver is adapted. The sub-carbonate will rise, and be condensed in the receiver in the form of a white crust.

(c) This sub-carbonate does not attract moisture from the air, but,

on the contrary, loses weight.

(d) Sub-carbonate of ammonia, like those of potash and soda, con-

verts vegetable blue colours to green, as the pure alkalies do.

(e) It requires for solution rather more than twice its weight of cold water, or an equal weight of boiling water. At the latter temperature, however, it is partly decomposed, and a violent effervescence ensues.

(f) In composition it varies considerably, according to the temperature in which it has been formed. Thus, sub-carbonate of ammonia, which has been produced in a temperature of 300° Fahrenheit, contains 50 per cent. of alkali; while carbonate formed at 60° contains only 20 per cent. By Gay Lussac\*, the sub-carbonate of ammonia is stated to consist of

Ammonia Carbonic acid					-	
	-	<b>-</b> .				
	100			007 5		470 57

<sup>\*</sup> Memoires d'Arcueil, ii. 214.

Dr. Ure has lately shown that the most compact and recent subcarbonate of ammonia contains water, which becomes apparent when it is distilled in mixture with dry pulverized quicklime\*. This water, he apprehends, constitutes an essential part of the alkaline base, which, in this view of it, is a hydrate of ammonia: and the same view may be extended to the other ammoniacal salts. The proportions of the sub-carbonate, deduced by him from a variety of experiments, are

			100.
Water	•	٠	15.
Carbonic Acid			
Ammonia			

Or we may consider the sub-carbonate as consisting of 54.5 acid and 45.5 hydrate of ammonia. By exposure to the air, the proportions of its elements are constantly changing, and its power of saturating acids decreased.

(g) It is decomposed by pure potash and pure soda; and by the sub-carbonates of those alkalies, which attract its carbonic acid, and expel the alkali. Hence it has been recommended, by Berthollet, to employ this salt for the full saturation of potash with carbonic

acid, which may be accomplished by the following process.

To a filtered solution of four pounds of pearlash in four quarts of water, add one pound of carbonate of ammonia, reduced to powder; and stir the mixture at intervals, till the carbonate of ammonia is entirely dissolved. Filter the liquor, and put it into a retort, which may be set in a sandbath, and be connected with a receiver. A very gentle heat is to be applied; so as to distil off about half a pint of the liquor, which will consist of a solution of carbonate of ammonia in water. The liquor in the retort may either be allowed to cool in it, or be transferred into a flat evaporating dish of Wedgwood's ware. When cold, crystals of the bi-carbonate of potash will probably be formed; otherwise another portion must be distilled off, and this must be repeated till the crystals appear; separate the first crystals that are formed; and, on repeating the distillation and cooling, fresh sets will appear in succession. A considerable portion of the solution, however, will refuse to crystallize. This may be boiled to dryness, and applied to the purposes of sub-carbonate of potash. The crystals of carbonate of potash may be washed with a small quantity of cold water and dried on blotting paper; or, if they are required of great purity, they may be dissolved in cold water, and re-crystallized, using the gentlest heat possible in evaporating the solution.

The NEUTRAL CARBONATE OF BI-CARBONATE OF AMMONIA was formed by Berthollet, by impregnating a solution of sub-carbonate with carbonic acid gas. According to his experiments, it is composed of

Thomson's Annals, x. 206.

Ammonia Carbonic acid	_				
	100.		355		139.2

From the known specific gravity of those two bodies, Gay Lussac has calculated that the neutral carbonate consists of exactly equal quantities by measure of the two gases, while the sub-carbonate is composed of two volumes of alkaline gas to one of carbonic acid gas.

The bi-carbonate of ammonia may also be formed by exposing powdered sub-carbonate with a larger and frequently renewed surface to the air, till it entirely loses its smell. In this state it is com-

posed, according to Dr. Ure, of

Carbonic	ac	id	•				54.5
Ammonia					•		<b>22.</b> 8
Water .							22.75*

The sub-carbonate, by this treatment, has its saturating power so much diminished, that 100 grains no longer neutralize 88 of concentrated sulphuric acid, but only 66. It may be doubted, however, whether, when thus obtained, it is not a mixture of sub-carbonate and bi-carbonate, since the acid and alkali are not in the proportions to each other, which are given in the analysis of Berthollet.

# ART. 4.—Carbonate of Barytes.

I. Pure barytes has a very powerful affinity for carbonic acid.

1. Let a solution of pure barytes be exposed to the atmosphere. It will soon be covered with a thin white pellicle; which when broken, will fall to the bottom of the vessel, and be succeeded by another. This may be continued, till the whole of the barytes is separated. The effect arises from the absorption of carbonic acid, which is always diffused through the atmosphere, and which forms with barytes a substance, viz. carbonate of barytes, much less soluble than the pure earth.

2. Blow the air from the lungs, by means of a quill, a tobacco-pipe, or glass tube, through a solution of barytes. The solution will im-

mediately become milky, for the same reason as before.

3. With a solution of pure barytes, mingle a little water, impregnated with carbonic acid. An immediate precipitation of carbonate of barytes will ensue.

4, Barytes has so strong an affinity for carbonic acid, as even to take it from other bodies. To a solution of a small portion of car-

\* Thomson's Annals, x. 207. There appears to be some error, since the numbers do not make up 100.

bonate of potash, of soda, or of ammonia, add the solution of barytes. The barytes will separate the carbonic acid from the alkali, and will fall down in the state of a carbonate. By adding a sufficient quantity of a solution of barytes in hot water, the whole of the carbonic acid. may thus be taken from a carbonated alkali; and the alkali will re main perfectly pure.

11.—1. Carbonate of barytes is nearly insoluble in water, which, at 60°, does not take up more than  $\frac{1}{4300}$  part, or, when boiling, about 2300. Water impregnated with carbonic acid dissolves a con-

siderably larger proportion.

2. Carbonate of barytes is perfectly tasteless, and does not alter

vegetable blue colours. It acts as a violent poison.

3. The combination of carbonic acid with barytes may either be formed artificially, as in the manner already described, and by other processes, to be detailed in the sequel, in which case it is termed, the artificial carbonate: or it may be procured, ready formed, from the earth, and is then called the native carbonate. It is not, however, a very common production of nature. The largest quantity, hitherto discovered, is in a mine, now no longer worked, at Anglezark, near Chorley, in Lancashire.

4. The native and artificial carbonates differ in the proportion of their components. The former contains, in 100 parts, 20 acid and 80 barytes. The artificial, according to Pelletier, consists of 22 acid, 62 earth, and 16 water; but in this statement, there is probably an error, since the proportions between the acid and earth differ considerably from those which have been determined by other chemists. ly speaking both the native and artificial compounds are sub-carbopates; but as we are unacquainted with any other compound of barytes and carbonic acid, they may be allowed to retain the accustomed name of carbonate. The latest analyses of this compound by Mr. Aikin, Mr. James Thomson\*, and others, fix its composition as

Mows:	Carb. acid.	Barytes.
From Mr. Aikin's experiments		
———Thomson's · · · · ·		
Klaproth and Rose's	. 22.00	. 78.00
Bucholz's	. 21.00	. 79.00
Berzelius'st	. 21.60	. 78.40
Dr. Wollaston (from theory).	. 22.09	. 77.91
When 100 grains of the carbonate are dis	ssolved in nitric	acid, and

precipitated by a sulphate, they afford, according to Berzelius, 118.6

or 119 grains of sulphate of barytes.

5. Carbonate of barytes is decomposed by an intense heat; its carbonic acid being expelled: and the barytes remaining pure. artificial carbonate is most readily decomposed; but the native one is generally employed for obtaining pure barytes, because it may be had in considerable quantity. The process which I have found to nswaer best, is nearly that of Pelletier. Let the native carbonate be

Nicholson's Journal, xxii. xxiii.

<sup>†78</sup> Ann. de Chim. 29.

powdered, and passed through a fine sieve. Work it up with about an equal bulk of wheaten flour into a ball, adding a sufficient quantity of water. Fill a crucible of proper size, about one third its height, with powdered charcoal; place the ball on this; and surround and cover it with the same powder, so as to prevent its coming into contact with the sides of the crucible. Lute on a cover; and expose it, for two hours, to the most violent heat that can be raised in a wind furnace. Let the ball be removed when cold. On the addition of water it will evolve great heat, as already described (chap. viii.), and the barytes will be dissolved. The filtered solution, on cooling, will shoot into beautiful crystals.

Carbonate of barytes is decomposed by the sulphuric, nitric, muriatic, and various other acids, which detach the carbonic acid,

and combine with the earth.

## ART. 5.—Carbonate of Strontites.

The relation of strontites to carbonic acid resembles, very closely, that of barytes; and all the experiments, directed to be made with the solution of the latter earth, may be repeated with that of stron-

tites, which will exhibit similar appearances.

The carbonate of strontites requires for solution 1536 parts of boiling water. It is found native, but containing a little cabonate of lime, at Strontian in Argyleshire; and may, also, be prepared by artificial processes, which will be afterwards described. From this carbonate pure strontites may be prepared, by treating it in the same manner as was directed for the calcination of carbonate of barytes.

The artificial carbonate, according to Stromeyer\*, does not essenti-

ally contain any water. It consists of

Strontites - - - - - 70.313 or 100 Carbonic acid - - - - 29.687 . . 42.22

100.

# ART. 6.—Carbonate of Lime.

1 Lime has a strong attraction for carbonic acid, but not when

perfectly dry.

(a) If a piece of dry quicklime be passed into a jar of carbonic acid gas over mercury, no absorption ensues. But invert a bottle, filled with carbonic acid gas, over a mixture of lime and water of the consistence of cream, and a rapid absorption will be observed, especially if the bottle be agitated.

(b) Let a jar or bottle, filled with carbonic acid, be brought over a vessel of lime water. On agitating the vessel, a rapid diminution

will ensue, and the lime water will become milky.

(c) Leave a shallow vessel of lime water exposed to the air. A white crust will form on the surface, and this if broken, will fall to the bottom, and be succeeded by another. This is owing to the absorption of carbonic acid gas from the air by the lime, which is thus rendered insoluble in water.

<sup>\*</sup> Ann. de Chim. et Phys. iii. 396.

(d) Lime, when exposed to the atmosphere, first acquires moisture, and then carbonic acid; and in a sufficient space of time, all

the characters distinguishing it as lime disappear.

(e) Lime has an extremely strong affinity for carbonic acid, which enables it to take this acid from other substances. Thus carbonates of alkalies are decomposed by lime. Slack a given quantity of lime into a paste with water, and add half its weight of carbonate of potash or soda. Boil the mixture, for half an hour, in an iron kettle, and separate the liquid part by filtration or by subsidence. The carbonic acid combines with the lime, and the alkali is obtained in a state of solution perfectly free from carbonic acid. This is the ordinary mode of depriving the alkalies of carbonic acid.

(f) Lime, when saturated with carbonic acid, must necessarily form bi-carbonate of line. We are unacquainted, however, with this salt, and it is chiefly by a process of reasoning that Berthollet has shown it must consist of 100 parts of lime united to 150.6 carbonic acid; whereas in the sub-carbonate 100 parts of lime are combined with only half that quantity\*. Of this, common chalk, or Carrara marble, may be taken as a fair sample; and in all sub-carbonates of this earth, we find the characters of insipidity and insolubility in water. Calcareous spar, marble, stalactites, lime-stone, and chalk, are all varieties of sub-carbonate of lime. It contains per cent.

According to Wollaston	_	_	-	43.7	_	-	-	56.3
Berzelius -								
— Dr. Ure -	-	-	-	43.52	-	-	-	56.48

It appears to be constituted of an atom of lime united with an atom of carbonic acid.

(g) Carbonate of lime is decomposed by a strong heat. If distilled in an earthen retort, carbonic acid gas is obtained, and lime remains in the retort in a pure or caustic state. By this process it loses about 45 per cent.

The very curious and important experiments of Sir James Hall have proved, that when the escape of the carbonic acid is prevented by strong pressure, carbonate of lime is fusible in a heat of about 22° of Wedgwood's pyrometer. And Mr. Bucholz has lately fused this substance, by the sudden application of a violent heat, without

additional compressiont.

(h) Carbonate of lime is decomposed by the stronger acids. Put some chalk into a gas bottle, and pour on it diluted sulphuric acid. The sulphuric acid will unite with the lime, and the carbonic acid will be set at liberty. One hundred grains of carbonate of lime, according to Pfaff, are saturated by 88 grains of sulphuric acid of the specific gravity 1854; and give 129.4 of sulphate of lime. These numbers, however, are not consistent with the known composition of carbonate and sulphate of lime, which requires that 100 grains of the carbonate should be saturated by 97.5 of oil of vitriol of the specific gavity 1850, and that there should result 136 of calcined sulphate of lime.

Memoires d'Arcueil, ii. 478.
 Nicholson's Journal, xiii. xvi.
 Nicholson's Journal, xvii. 229.

By a comparison of this experiment with the preceding one (g), we may learn the proportion of carbonic acid and water contained in any carbonate of lime. Let 100 grains of the carbonate be put into a Florence flask, with an ounce or two of water; place this in the scale of a balance; and in the same scale, but in a separate bottle, about half an ounce of muriatic acid. Add the muriatic acid to the carbonate as long as any effervescence is produced, and then blow out the disengaged carbonic acid, which remains in the flask, by a pair of bellows. Ascertain, by adding weights to the opposite scale, how much has been lost; suppose it to be forty grains; this shows the quantity of carbonic acid disengaged. Calcine another 100 grains in a covered crucible. It will lose still more of its weight; because, besides its carbonic acid, all the water is expelled which it may contain. Let this loss be stated at 45 grains; the former loss deducted from this (45-40), or 5 grains, shows the quantity of water in 100 of the carbonate.

(i) Carbonate of lime, though scarcely disolved by pure water, is soluble in water saturated with carbonic acid. The most striking method of showing this is the following: Add to a jar, about one fourth filled with lime water, a very small quantity of water saturated with carbonic acid. An immediate milkiness will ensue, because the carbonic acid forms with the lime an insoluble carbonate. Add gradually more of the water, impregnated with carbonic acid, shaking the jar as these additions are made. At last the precipitate is re-dissolved. Hence it appears that lime, with a certain proportion of carbonic acid, is insoluble, and, with a still larger, again be-

comes soluble in water.

(k) The carbonate of lime, dissolved by an excess of carbonic acid (i), is again separated, when this excess is driven off. Thus boiling, which expels the superabundant acid, precipitates the carbonate. Caustic, or pure alkalies, also produce a similar effect.

# ART. 7.—Carbonate of Magnesia.

I. Pure magnesia does not attract carbonic acid with nearly the same intensity as lime. Hence magnesia may be exposed to the air, without any important change in its properties, or much increase of weight, unless the exposure be long continued, when it first becomes a hydrate by absorbing water, and then attracts carbonic acid from the atmosphere. The carbonate of magnesia, used in medicine, and for experimental purposes, is prepared by a process to be described in the sequel. In this state, however, it is not entirely saturated with carbonic acid, and is rather a sub-carbonate. Its composition Bucholz states to vary, and is prepared with or without heat. If the former, it contains per cent. 42 base, 35 acid, 23 water; if prepared from cold solutions of sub-carbonate of soda and sulphate of magnesia, it consists of 33 base, 32 acid, and 35 water. Mr. Dalton makes it to be composed of 43 base, 40 acid, and 17 water, which numbers indicate that it is constituted of one atom of acid, one of earth, and one of water. Berzelius is of opinion that it is a compound of three atoms of carbonate of magnesia with one atom of

the hydrate of the same earth\*.

may be obtained, by passing streams of carbonic acid gas through water, in which the sub-carbonate is kept mechanically suspended. The solution yields, when evaporated, small crystals, which are transparent hexagonal prisms, terminated by hexagonal planes. These crystals have no taste, and are soluble in 48 parts of cold water; whereas the sub-carbonate requires at least ten times that quantity. The crystallized carbonate contains per cent. 30 acid, 30 earth, and 40 water, so that it is in reality constituted like the common carbonate, but with three atoms of water instead of one.

III. The carbonate of magnesia is decomposed by the same agents as the carbonate of lime. It yields its carbonic acid, however, in a

much more moderate heat.

IV. Lime has a stronger affinity than magnesia for carbonic acid. Hence, if lime water be digested with carbonate of magnesia, the lime is precipitated in the state of an insoluble carbonate.

## ART. 8 .- Carbonate of Glucine.

Glucine appears to have a considerable affinity for carbonic acid; for, when precipitated from acids by pure alkalies, and dried in the air, it becomes effervescent. The carbonate of glucine is white, insipid, insoluble, and very light. It contains about one fourth its weight of carbonic acid, which it loses by exposure to a low red heat.

The carbonate of silex dose not exist, and those of zircon, alumine, and yttria, have no peculiarly interesting properties.

#### SECTION V.

# Gaseous Oxide of Carbon, or Carbonous Oxide.

This combination of carbon with oxygen contains a less proportion of oxygen than is found in carbonic acid. Its discovery was announced in Nicholson's Journal, for April, 1801, by Mr. Cruickshank, and in the 38th volume of the Annales de Chimie, by Clement and Desormes, whose experiments are continued in the 39th volume of the same work, p. 26. The Dutch chemists, however, in volume 43, object to its being considered as a distinct gas, and regard it merely as a carburet of hydrogen. But their objections do not appear sufficient to prevent the acknowledgment of the gaseous oxide as a new and peculiar species.

It may be procured by the following processes.

1. By the distillation of the white oxide of zinc with one eighth of its weight of charcoal, in an earthen or glass retort; from the scales which fly from iron in forging, mixed with a similar proportion of char-

<sup>\*.</sup> Thomson's Annals, xii. 30.

coal; from the oxides of lead, mangnese, or, indeed, of almost every imperfect metal, when heated in contact with powdered charcoal. It may also be obtained from the substance which remains after preparing agetic acid from acetate of copper.

2. From well dried carbonate of barytes or of lime (common chalk). distilled with about one fifth of charcoal; or with rather a larger proportion of dry iron or zinc filings, which afford it quite free from

hydrogen.

3. By transmitting carbonic acid gas over charcoal ignited in a porcelain tube. The acid gas combines with an additional dose of charcoal; loses its acid properties; and is converted into the carbonous oxide. An ingenious apparatus, contrived by M. Baruel, and extremely useful for this and similar purposes, is described and represented by a plate, in the 11th volume of Nicholson's Journal.

The last product of the distillation is the purest, but still contains carbonic acid, which must be separated by washing the gas with

lime liquor.

Its properties are as follow: (a) It has an offensive smell.

- (b) It is lighter than common air, in the proportion of 966 to 1000. One hundred cubical inches weigh 30 grains, the temperature being 55° Fahrenheit, and pressure 29.5 (Cruickshank); or at temperature 60°, and barometer 30, 100 cubic inches weigh 30.19 grains. Its specific gravity from calculation, according to Gay Lussac, should be .96782.
- (c) It is inflammable, and, when set fire to, as it issues from the orifice of a small pipe, burns with a blue flame. When mixed with common air, it does not explode like other inflammable gases, unless in very few proportions\*, but burns silently with a lambent blue flame. A mixture of two measures with one measure of common air may, however, be exploded by a lighted taper, or even by redhot iron or charcoal.
- (d) When a stream of this gas is burnt, in the manner described in speaking of hydrogen gas, no water is condensed on the inner surface of the glass globe, a proof that the gaseous oxide contains no Berthollet, indeed, still contends, in opposition to most chemists (and among others to Gay Lussac), that hydrogen is one of the elements of this gas.

(e) It is sparingly soluble in water; is not absorbed by liquid caus-

tic alkalies; nor does it precipitate lime water.

(f) It is extremely noxious to animals; and fatal to them if confined in it. When respired for a few minutes, it produces giddiness

and faintingt.

(g) When 100 measures of carbonous oxide are fired over mercury in a detonating tube, with 45 of oxygen gas, the total 145 are diminished to 90, which, if the gasses employed be pure, consist entirely of carbonic acid. Proportions, differing a little from these, have been stated by Berthollet, viz. that 100 measures of carbon-

<sup>\*</sup> Dalton's System, p. 373.

ous oxide are saturated by 50 measures of oxygen, and give 100 of carbonic acid; and these last proportions are coincident, also, both with the theory and experience of Gay Lussac.

(h) It is not expanded by electric shocks, nor does it appear to

undergo any change by electrization.

(i) When the carbonous oxide, mingled with an equal bulk of hydrogen gas, is passed through an ignited tube, the tube becomes lined with charcoal. In this temperature, the hydrogen attracts oxygen more strongly than it is retained by the charcoal, and forms water.

It was found, also, by Gay Lussac to be decomposed by the action of potassium, which combines with the oxygen and precipitates char-

coal.

According to Mr. Cruickshank, it contains per cent. about 70 oxygen, and 30 carbon by weight; or the former is to the latter as 21 to 8.6, or as 21 to 9. Gay Lussac, however, makes it to consist of 43 charcoal and 57 oxygen; Berzelius of 44. 28 charcoal and 55.72 oxygen, proportions which agree, within a small fraction, with those of Clement and Desormes. It contains, therefore, just half the oxygen that exists in carbonic acid; and it is constituted of one atom of charcoal and one atom of oxygen, and weighs, according to Mr. Dalton, 7 + 5.4 = 12.4, or, by the corrected numbers, 7.5 + 5.8 = 13.3.

#### SECTION VI.

# Combination of Carbon with Hydrogen, forming Carbureted Hydrogen Gas, or Hydro-Carburet.

I. Or this combination there appear, on first view, to be several distinct varieties, consisting of carbon and hydrogen, united in va-

rious proportions, and obtained by different processes.

1. When the vapour of water is brought into contact with redhot charcoal (by means of an apparatus similar to that represented, fig. 40), two different products are obtained. The oxygen of the water, uniting with the carbon, constitutes carbonous oxide and carbonic acid; and the hydrogen of the water dissolving, at the moment of its liberation, a portion of charcoal composes carbureted hydrogen gas \*.

The carbonic acid may be separated from the hydro-carburet, by agitating the gas, which has been produced, in contact with lime and water, mixed together, so as to be of the consistence of cream.

2. By stirring, with a stick, the mud that is deposited at the bottom of ditches or stagnant pools, bubbles of gas ascend to the surface, and may be collected in an inverted bottle of water, to the mouth of which a funnel, also inverted, is fixed.

3. By submitting coal to distillation, in an iron or coated glass retort, a large quantity of gas, besides a portion of tar, is produced. The latter may be received in an intermediate vessel; and the gas

<sup>\*</sup> In Nicholson's Journal, xi. 68, I have stated my reasons for believing that this gas is not pure hydro-carburet.

must be well washed with lime liquor. The first product only is to be reserved as a specimen of coal gas; for, as the distillation proceeds, its density become gradually less; till, at length, the gas, which is produced at the close of the operation, is only about half as heavy as that evolved at first. The quantity of gas, also, which is produced from a given weight of coal, is so variable from different kinds of this mineral, and is so much influenced by the degree of heat employed in its production, that it is scarcely possible to state any general average. From 120 pounds avoirdupois of the sort of coal called Wigan Cannel, about 340 cubic feet of gas may be obtained, of which half a cubic foot per hour is equal to a mould candle of six to the pound, burning during the same space of time.

4. Let a porcelain tube, coated with clay, be fixed horizontally in a furnace, in the manner represented, fig. 40. To one end let a retort be luted, containing an ounce or two of ether or alcohol; and, to the other, a bent tube, which terminates under the shelf of the pneumatic trough. A gas will be disengaged, on igniting the tube, and transmitting, through it, the alcohol or ether in vapour, which,

when washed with lime-liquor, is the carbureted hydrogen.

5. A fifth mode of obtaining hydro-carburet, discovered by the Dutch chemists\*, consists in distilling, in a glass retort, with a gentle heat, three measures of concentrated sulphuric acid, and one measure of alcohol. The mixture assumes a black colour and thick consistence; and bubbles of gas are disengaged, which may be collected over water. For reasons which will be stated when we come to

speak of chlorine, this gas has been named the olefiant gas.

II.—1. These different gases vary considerably, in density or specific gravity. Atmospheric air being 1000, the specific gravity of gas from moistened charcoal is 480; from ether or alcohol 520; from pit-coal between 300 and 780, according to the period of the distillation, at which it is collected, the early products being always the heaviest. Gas from stagnant water, according to Mr. Dalton, is of the specific gravity 600, and hence 100 cubic inches must weigh 18.3; but Dr. Thomson fixes its specific gravity at 555, which would give only 16.93 grains for 100 cubic inches. The specific gravity of olefiant gas is stated by the Dutch chemists, its discoverers, at 909, by Dalton and Henry at 967 or 950, by Saussure at 978.4, by Dr. Thomson at 974; and by Gay Lussac, from calculation, at 978. From the last number, the weight of 100 cubic inches at 60° Fahrenheit, and 30 inches barometer, may be deduced to be 29.72 grains.

2. These gases differ as to the quantity, which water is capable of absorbing; for of the olefant gas it takes up the of its bulk; of

gas from stagnant water 1, and of the others still less.

3. The varieties of carbureted hydrogen gas all agree in being inflammable; but they possess this property in various degrees, as is evinced by the variable brightness of the flame, which they yield when set on fire; and by the different temperatures at which they begin to burn. Light carbureted hydrogen, or fire-damp, requires

<sup>\*</sup> Nicholson's Journal, 4to. i. 41

a much stronger heat to excite its combustion than olefant gas. They may be inflamed as they proceed from the orifice of a small pipe, or from between two concentric cylinders of sheet-iron or copper, placed at the distance of a small fraction of an inch from each other. On this principle, an Argand's lamp may be constructed, for burning the gases, which will issue from that space, commonly

occupied by the wick.

When burned in either of these modes, there is a manifest gradation in the density and brightness of the flame, corresponding to the quantity of solid charcoal which is first deposited, and afterwards burned. The gas from charcoal burns with a faint blue light, not suited to the purpose of illumination; that from ether or alcohol with more brilliancy; but still short of that with which the coal gas burns, when recently prepared; and the first product of gas from a given quantity of coal, affords at least twice as much light, as an equal volume of the last portions. The olefiant gas surpasses them all, in the quantity of light evolved by its combustion. It continues to burn in air, the density of which is diminished 10 or 11 times, whereas gas from stagnant water affords a flame, which is extinguished in air rarefied more than one fourth. Another important distinction between the several kinds of carbureted hydrogen is derived from the results of mixing each of them with chlorine, which will be described in the chapter on that substance.

If these gases be burned in a vessel of oxygen gas over lime-water, by means of a bladder and bent brass pipe (pl. iv. fig. 41), two distinct products are obtained, viz. water and carbonic acid. That water is produced, may be shown by burning a very small stream of this gas, under a long funnel-shaped tube open at both ends. The formation of carbonic acid is evinced, by the copious precipitation

of the lime-water in the foregoing experiment.

The composition of each of the above gases is learned by firing it, in a detonating tube over mercury, with a known quantity of oxygen gas; and observing the nature and quantity of the products. These products are carbonic acid and water. The former may be exactly measured; but the water is generated in such small quantity, that it can only be computed. The following table shows the results of a few experiments of this kind.

Kind of Gas.				easur as red ite 10	qui	red t	Measures of Carbonic Acid produced.				
Pure hydrogen gas				50	to	54					
Gas from charcoal				60					•	. 35	
coal											٠.
	•	é	•	200	٠	•		•	•	100	
Olefiant gas	•	•	•	300	•	•	•	•	•	200	

Now since, for the formation of each measure of carbonic acid gas, in the foregoing experiments, an equal volume of oxygen gas is required, we may learn by deducting the number in the third column from the corresponding one in the second, what proportion of oxygen

has been spent in the saturation of the hydrogen of each variety of hydro-carburet. Thus for example, in burning the gas from stagnant water, 100 measures of oxygen have been employed in forming carbonic acid; and the remaining 100 in saturating hydrogen. But 100 measures of oxygen are sufficient to saturate 200 of hydrogen gas; and a quantity of hydrogen must therefore be contained in 100 measures of gas from stagnant water; which, expanded to its usual elasticity, would occupy 200 measures.

From these data, it is easy to deduce the composition of this variety of carbureted hydrogen; for if its specific gravity be 0.6,

. A	•
100 cubic inches must weigh The 100 cubic inches of carbonic acid produced weigh 47 grains, and contain of charcoal	Grains. 18.3 13.2
Hence the hydrogen, in 100 cubic inches, weighs	5.1
Or 100 grains of gas from stagnant water are composed of	•
Carbon 72	
Hydrogen 28	

Hydrogen - - - 28 100

These results accord best with the opinion that this gas, which may be called simply carbureted hydrogen, is constituted of one atom of charcoal and two atoms of hydrogen.

Olefiant gas, per-carbureted hydrogen, or bi-carbureted hydrogen, investigated in precisely the same manner, is composed, in 100 grains,

			(	Carbo	n.			Hyd	lrogen.
According to Dr. Thomson*, of	-	-	-	85	-	-	-	-	15
Saussure, inn. of	-	-	_	86	-	-	_		14

It consists, therefore, according to Mr. Dalton, of one atom of carbon and one atom of hydrogen. This would make the weight of an atom of charcoal 5.66; for 85 is to 15, as 5.66 to 1; a result which coincides, as nearly as can be expected, with the weight of the atom of charcoal, already deduced from the composition of carbonic acid, viz. 5.65.

The only distinct and well characterized species of carbureted hydrogen appear to me to be olefiant gas, or per-carbureted hydrogen; and the gas from stagnant water, called simply carbureted hydrogen, to which the epithet light is prefixed by some chemists, on account of its inferior specific gravity. Of these, with occasionally a portion of carbonic oxide, and other inflammable gases, the other varieties appear to be mixtures. The coal gas, for example, which is now so generally used for the purpose of affording light, I have shower to be a mixture of at least five others, the proportion of which varies at every successive stage of the distillation of coal. It has been con-

<sup>\* 37</sup> Phil. Mag. 260. · Vol. I.—K k

<sup>†</sup> Phil. Tpans. 1808.

tended, indeed, by Berthollet, Murray, and other philosophers, that carbon and hydrogen are capable of uniting in a variety of proportions, not only with each other, but with oxygen. But there seems reason to believe, from a careful examination of all the best experiments on these compounds, that hydrogen and carbon unite only in two definite proportions, and that these proportions are no other, than those constituting carbureted and per-carbureted hydrogen gases, viz. in the former one atom of charcoal to two atoms of hydrogen, and in the latter an atom of each of those combustible bodies.

On the Fire Damp of Coal Mines, and the Construction and Principle of the Safety-Lamp of Sir H. Davy.

The fire-damp of coal mines, by an analysis of it which I published in 1806, was shown to be identical in composition with light carbureted hydrogen\*. This conclusion coincides with the subsequent results of Sir H. Davy, who has enlarged our knowledge of the chemical history of the fire-damp, by several important factst. The most readily explosive mixture of fire-damp with common air he found to be one measure of the gas to seven or eight of air. This mixture was not set on fire by charcoal in a state of active combustion, nor by iron ignited to a red or even to a white heat, except when in a state of brilliant combustion; in which respects, the fire-damp differs from other combustible gases.

It was in attempting to measure the expansion, occasioned by the combustion of a mixture of fire-damp and air, that Sir H. Davy discovered a fact, which afterwards led him to the most novel and important results. An explosive mixture could not, he ascertained, be kindled in a glass tube so narrow as \frac{1}{7} of an inch diameter; and when two separate reservoirs of an explosive mixture were connected by a metallic tube, \frac{1}{3} of an inch diameter and 1\frac{1}{2} inch in length, and one of the portions of gas was set on fire, the explosion did not extend to the other. Fine wire sieves or wire gauze, interposed between two separate quantities of an explosive mixture, were also found to prevent the combustion of one portion from apreading to the other. A mixture of fire-damp and air in explosive proportions, was deprived of its power of exploding by the addition of about \frac{1}{7} its bulk of carbonic acid or nitrogen gas.

Reflection on these facts suggested to Sir H. Davy the possibility of constructing a lampt, in which the flame, by being supplied with only a limited quantity of air, might produce carbonic acid and nitrogen in such proportion as to destroy the combustibility of explosive aixtures; and which might, also, by the nature of its apertures for giving admittance and exit to the air, be rendered incapable of

Hunter, 1818.

<sup>\*</sup> Nicholson's Journal, xix. 149. † Phil. Trans. 1816. † A full history of the Safety Lamp, and of the chemical researches connected with it, has lately been published by Sir H. Davy, 8vo. printed for R.

spreading combustion to the surrounding atmosphere, supposing this to be an inflammable one.

This most desirable object was accomplished by the use of airtight lanterns, supplied with air through tubes or canals of small diameter, or through apertures covered with wire gauze below the flame, and having a chimney at the upper part on a similar system, for carrying off the foul air. The apparatus was afterwards simplified, by covering or surrounding the flame of a lamp or candle with a cylindrical wire sieve, having at least 625 apertures in a square inch. Within this cylinder, when the fire-damp encompassing it is to the air as 1 to 12, the flame of the wick is seen surrounded by the feeble blue flame of the gas. When the proportion is as 1 to 5, 6, or 7, the cylinder is filled with the flame of the fire-damp; but though the wire gauze becomes red-hot, the exterior air, even when explosive, is not kindled. The lamp is therefore safe in the most dangerous atmospheres, and has been used most extensively in the mines of Whitehaven, New-castle, and other places, without the occurrence of a single failure or accident.

The effect of the safety-lamp depends on the cooling agency of the wire gauze, exerted on the portion of gas burning within the cylinder. Hence a lamp may be secure where there is no current of an explosive mixture to occasion its being strongly heated; and yet not safe, when the current passes through it with great rapidity. But any atmosphere, however explosive, may be rendered harmless, by increasing the cooling surface; which may be done, either by diminishing the size of the apertures, or by increasing their depth, both of which are perfectly within the power of the manufacturer of

the wire gauze.

When a small coil of platinum wire is hung above the wick of the lamp within the wire gauze cylinder, the metal continues to glow, long after the lamp is extinguished, and affords light enough to guide the miner in what would otherwise be impenetrable darkness. In this case, the combustion of the fire damp is continued so slowly, and at so low a temperature, as not to be adequate to that ignition of gaseous matter which constitutes flame, though it excites a temperature sufficient to render platinum wire luminous. A similar ignition of platinum wire, it has lately been found, may be supported for many hours, by surrounding the flame of a spirit lamp with small coils of that metal, not exceeding its of an inch in diameter. Twelve coils of this wire, twisted spirally round the tube of a tobacco pipe, or round any thing that will render the coils about 30 of an inch in diameter, are to surround, six the wick of the lamp, and six to remain elevated above the wick. The wick should be small, and quite loose in the burner of the lamp; and the fibres of the cotton, surrounded by the coil, should be laid as strait as possible. When the lamp, after being lighted for a few moments, is blown out, the platinum wire continues to glow for several hours, as long as there is a supply of spirit of wine, and to give light enough to read by; and sometimes the heat produced is sufficient to re-kindle the lamp spontaneously\*.

<sup>\*</sup> Thomson's Annals, vol. xi.

#### SECTION VII.

## Carburet of Nitrogen, or Cyanogen.

To obtain cyanogen, it is necessary first to prepare a pure prussiate of mercury, by boiling fine powdered red oxide of mercury with twice its weight of prussian blue and a sufficient quantity of water. The compound is perfectly neutral, and crystalizes in long four-sided prisms truncated obliquely. It still, however, contains a little iron. which may be separated by digesting the liquor, before evaporation, with a little more of the oxide of mercury, and saturating the excess of this oxide with a little prussic acid (see vol. ii.), or even with a lit-The prussiate of mercury, thus obtained, must be tle muriatic acid. completely dried at a temperature below that of boiling water, and then exposed to heat in a small retort, or in a tube closed at one extremity. It first blackens, then liquifies, and the cyanogen comes over in the form of a gas, which may be collected over mercury. In the retort there remains a charry matter of the colour of soot, and as light as lamp black\*.

1. Cyanogen is a true gas, or permanently elastic fluid. Its smell is strong and penetrating. It burns with a bluish flame mixed with purple. Its specific gravity is to that of common air as 1.8064 to 1.

Hence 100 cubic inches at 60° Fahr. weigh 55 grains.

2. Water at the temperature of 60° Fahr. absorbs almost 44 times

its volume, and pure alcohol 23 times its volume.

3. When 100 measures of cyanogen are detonated, in a Volta's eudiometer, with 250 measures of oxygen gas, 200 measures of carbonic acid result; and 100 measures of nitrogen. There remain, also, 50 measures of oxygen gas uncondensed. From these data, it is calculated by Gay Lussac, that cyanogen is composed of two volumes of the vapour of charcoal and one volume of nitrogen, condensed into a single volume. Its density ought, therefore, to be 1.8011, a number not very remote from that obtained by experiment.

4. Analysis by more complicated methods afforded the same result, evincing that cyanogen yields by a decomposition effected by means of oxygen, twice its volume of carbonic acid and an equal volume of nitrogen. No water whatsoever is formed during its combustion, if the gas be perfectly free from prussic acid vapour, a suffi-cient proof of the absence of hydrogen from its composition.

5. The solutions of pure alkalies and alkaline earths absorb cyanogen; and the liquid obtained, when poured into a solution of black oxide of iron, affords prussian blue, but not without the addition of an acid. At the same time, carbonic acid gas escapes in volume equivalent to the cyanogen absorbed, and there is a perceptible smell of prussic acid. These changes will be more evident from the following recapitulation:

<sup>\*</sup> Gay Lussac, Ann. de Chim. vol. xcv.; or Thomson's Annals, viii. 37.

One volume of charcoal, uniting with one volume of oxygen, forms one volume of carbonic acid; the remaining volume of charcoal, uniting with half a volume of nitrogen and half a volume of hydrogen, composes prussic acid; and the residuary half volume of nitrogen and 1½ volume of hydrogen compose together one volume of ammonia,

6. It will afterwards be shown, that when to two volumes of charcoal and one volume of nitrogen, together constituting cyanogen, one volume of hydrogen is joined, and the whole condensed into two volumes, we obtain prussic acid. Cyanogen agrees then with chlorine and iodine, in being acidifiable by union with hydrogen. Hence its compounds with metallic bases have been called by Gay Lussac cyanures, as those of chlorine are called chlorures; but having elsewhere expressed a preference for the name of chlorides, I shall, from analogy, give to the compounds of cyanogen the name of cyanides.

#### CHAPTER XII.

SULPHUR.—SULPHURIC ACID.—SULPHATES.—BINARY COMPOUNDS OF SULPHUR.

In describing sulphur and its compounds, I shall take them in the following order:

I. Sulphur in its uncombined state.

II. Sulphur united with its full proportion of oxygen, constituting Sulphuric Acid; and the compounds of this acid with alkalies and

earths, termed SULPHATES.

III. Sulphur united with a less proportion of oxygen, composing sulphurous acid; and the compounds of this acid, called sulphures. It appears, also, from recent experiments, that there is a third acid, constituted of sulphur with a still less proportion of oxygen. This acid is at present known only in combination. It is called hyposulphurous of per-sulphurous acid.

IV. The compounds of sulphur with alkalies and earths, termed

SUPLHURETS.

V. The combination of sulphur and hydrogen, named SULPHURET-ED HYDROGEN; and the compounds, which it forms with alkaline

and earthy bases, called HYDRO-SULPHURETS.

VI. The compound of sulphureted hydrogen with a still farther quantity of sulphur, composing super-sulphureted hydrogen; and its compounds with different bases called hydrogureted sulphurets, or sometimes sulphureted-hydro-sulphurets.

#### SECTION I.

#### SULPHUR.

I. The sulphur, which occurs as an article of commerce, is a mineral production, and is brought to this country chiefly from Sicily.

That which is procured in our own island, is generally of very inferior quality, and contains a portion of the metal, from combination with which it has been separated. It is met with under two different forms; of a compact solid, which has generally the shape of long rolls or sticks; and of a light powder called flowers of sulphur. In general, the latter may be considered as most pure; but the two varieties, it will presently appear, are readily convertible into each other by the modified application of heat. Its specific gravity is 1.98 or 1.92.

II. Sulphur is readily fused and volatilized. When heated to 170° of Fahrenheit, it begins to evaporate, and to produce a very disagreeable smell; at 185° or 190° it begins to melt; and at 220° is completely fluid. If the heat be rapidly increased, it loses at 350° its fluidity, and becomes firm, and of a deeper colour. It regains its fluidity, if we reduce the temperature; and this may be repeated at pleasure, in close glass vessels, if the changes of heat be not slow;

otherwise it is volatilized. It sublimes at 600°.

III. If, after being melted, it be suffered to cool, it congeals in a crystalline form, but so confusedly, that we cannot define the shape of the crystals, farther than that they are slender interlaced fibres. If a large mass be kept fluid below, while it congeals at the surface, the crystallization there is much more distinct. When sulphur in complete fusion, viz. at 300°, is poured into water, it becomes tenacious like wax, and may be applied (as is done by Mr. Tassie) to take impressions from engraved stones, &c. These impressions are quite hard, when the sulphur has become cold. It is then of a red colour,

and of the specific gravity 2.325.

IV. At the temperature of about 290° Fahrenheit, sulphur is converted into vapour; and if this operation be conducted in close vessels, the volatilized sulphur is again collected in a solid form. What remains has been called sulphur vivum. This affords an example of the process of sublimation, which differs from distillation, in affording a solid product, while the latter yields a condensed liquid. In this mode, sulphur may, in part, be purified; and its purification is completed, by boiling it repeatedly in distilled water; then in twice or thrice its weight of nitro-muriatic acid, diluted with one part of distilled water; and, finally, by washing it with distilled water, till this comes off tasteless, and incapable of changing the blue colours of vegetables.

V. When flowers of sulphur are digested in alcohol, no union takes place; but if the two bodies be brought into contact, when both are in a state of vapour, they enter into chemical union. This may be shown by an ingenious experiment of La Grange, the apparatus for performing which is represented in the first plate of his "Manual." Into a glass alembic (see the plates to this work, fig. 2) put a little sulphur; over this suspend a small bot le filled with alcohol; and apply a receiver to the pipe of the alembic, the head being put into its place. Lute the junctures, and apply a gentle heat to the alembic. The sulphur will now be raised in vapour; and the vapour surrounding the bottle of alcohol, the latter will be volatilized, and will meet in this state the funes of sulphur. A combination will take place.

between the two bodies, and sulphurized alcohol will pass into the receiver. On pouring this preparation into water, the sulphur will

be precipitated.

VI. Though it had already been suspected (chiefly from the experiments of M. Berthollet, jun. described in sect. 6, art. 4, of this chapter) that sulphur contains hydrogen, yet the first unequivocal evidence of the fact was furnished by Sir H. Davy. A bent glass tube, having a platinum wire hermetically sealed into its upper extremity, was filled with sulphur. The sulphur was melted by heat; and a proper connection being made with the Voltaic apparatus of 500 double plates, each six inches square and highly charged, a most intense action took place. A very brilliant light was emitted; the sulphur soon entered into ebullition; elastic matter was evolved in great quantities; and the sulphur, from being of a pure yellow, became of a dark reddish brown tint. The gas was found to be sulphureted hydrogen, or hydrogen gas holding sulphur in solution; and its quantity, in about two hours, was more than five times the volume of the sulphur employed.

Another proof of the presence of hyd ogen in sulphur is derived from the action of potassium; for these two bodies combine with great energy, and evolve sulphureted hydrogen, with intense heat

and light.

Lastly, when dry sulphur is burned in dry oxygen gas, Sir H. Davy is of opinion that, besides sulphuric acid, a portion of water is also formed; but he is still doubtful whether the hydrogen in sulphur can be considered as any thing more than an accidental ingredient. This view of the subject is embraced, also, by Berzelius\*, who found, by heating sulphur with oxide of lead, that the quantity of water produced is much too minute to indicate any definite pro-

portion of hydrogen in sulphur.

Another ingredient of sulphur, it appeared probable from the experiments of Sir H. Davy, is oxygen. For potassium, after being made to act on sulphureted hydrogen gas, evolved less hydrogen from water, than it ought to have done. It has since, however, been proved by Gay Lussact, that when all sources of fallacy are avoided, a given weight of potassium, which has been exposed to sulphureted hydrogen, separates exactly the same volume of hydrogen gas from water, as an equal weight of recent metal. Potassium, therefore, acquires no oxygen from the sulphur, which is contained in sulphureted hydrogen.

VII. Sulphur is inflammable, and appears susceptible of two distinct combustions, which take place at different temperatures. At 140° or 150° Fahrenheit, it begins sensibly to attract oxygen; and if the temperature be raised to 180° or 190°, the combination becomes pretty rapid, accompanied by a faint blue light. But the heat evolved is scarcely sensible; at least it is so weak, that the sulphur may

<sup>\* 79</sup> Ann. de Chim. 119. † Ann. de Chim. vol. lxxiii. ‡ For an account of the oxides of sulphur, see Dr. Thomson's paper in Nicholsen's Journal, vi. 101.

thus be burned out of gunpowder, and the powder be rendered useless without inflaming it. At a temperature of 300°, its combustion, though still feeble compared with that of some other bodies, is much more active, and accompanied with a redder light. When set on fire in oxygen gas, it burns with a very beautiful and brilliant light; but of a given quantity of oxygen gas, it is not possible to condense the whole by this combustion, for reasons which hereafter will be stated. The product of these combustions, when examined, will be found to be sulphurous and sulphuric acid, but chiefly the former, and if water be carefully excluded, sulphurous acid only is formed. It is necessary, therefore, in order to produce sulphuric acid to make the experiment over water.

#### SECTION II.

### Sulphuric Acid.

The properties of this acid must be exhibited by a portion of that usually found in the shops. They are as follows:

(a) Sulphuric acid has a thick and oily consistence; as may be

seen by pouring it from one vessel into another.

(b) In a pure state, it is perfectly limpid and colourless.

(c) When mixed suddenly with water, considerable heat is produced. Four parts, by weight, of concentrated sulphuric acid, and one of water, when mixed together, each at the temperature of 50°

Fahrenheit, have their temperature raised to 300°.

When an ounce of water has been suddenly mixed with three of sulphuric acid, and the mixture been suffered to cool to the temperature of the atmosphere, an additional half oz. of water raises it to 86°. a second to 96°, and a third to 104°\*. The greatest elevation of temperature, Dr. Ure finds to be occasioned by the sudden mixture of 73 parts by weight of strong sulphuric acid with 27 of water. This rise of temperature takes place, because the affinity or capacity of the compound of sulphuric acid and water for caloric, is less than that of the acid and water separately. A diminution of bulk also ensues; that is, one measure of acid and one of water do not occupy the space of two measures, but about 15th less; and the greatest condensation results, when those proportions are used, which give the greatest increase of temperature. Owing to the heat produced by its admixture with water, the dilution for ordinary purposes, should be conducted very gradually; and the acid should be added to the water by small portions at once, allowing each portion to cool before a fresh addition is made. On the principle of its attraction for water is to be explained, also, the rapid increase of weight which the acid requires when exposed to air. In one day, three parts of sulphuric acid, exposed to the atmosphere, are increas-

<sup>\* 1</sup> Philips on the London Pharmac. p. 24.

ed in weight one part; and one ounce, by twelve months' exposure,

has been found to gain an addition of 64.

(d) Perfectly pure sulphuric acid remains quite limpid during dilution. The sulphuric acid, however, commonly found in the shops, under the name of oil of vitriol, on admixture with water, deposits a white powder, in considerable quantity, consisting of various impurities, but chiefly of sulphate of lead. Berzelius has found, also, a minute quantity of titanium in sulphuric acid of English manufacture, and tellurium in acid prepared at Stockholm\*. By evaporating sulphuric acid of commerce in a platinum dish, Dr. Ure has obtained from one half to three quarters of a grain in 100 of solid matter, consisting of about two parts of sulphate of potash and one of sul-

phate of leadt.

(e) Sulphuric acid is nearly twice as heavy as water. The specific gravity of the strongest pure acid that can be obtained, is 1.850: but even this contains 19 (according to Dr. Wollaston, 18.44) per cent. of water, which appears essential to its constitution, and can only be separated by combining the acid with a base. Dr. Ure states that genuine commercial acid should not exceed 1.8485. When denser, its purity may be suspected. It has been ascertained by Mr. Dalton, that acid, of nearly the maximum strength, has its specific gravity very little altered, by adding or subtracting small portions of water. Thus acids containing 81 and 80 per cent. of acid, do not differ more than 1 in the third place of decimals; nor is the specific gravity proportionally changed by dilution till it falls as low as 1.78. strength of the more concentrated acid may be better ascertained, by observing how much water is required, to bring it down to the specific gravity 1.78. The boiling point, also, Mr. Dalton has discovered, is a much better test of its strength; and he has constructed the following useful Table, in which account is taken of all these circumstances.

<sup>\*</sup> Thomson's Annals, x. 464. † Journ. of Science, iv. 115.

Mr. Dalton's Table of the Quantity of real Acid in 100 Parts of Liquid Sulphuric Acid, at the Temperature 60° Fahrenheit.

_	Atoms Acid Water.		Real Acid per cent. by Weight.	Real Acid per cent. by Measure.	Specific Gravity.	Boiling Point.			
	1 +	0	100	unknown.	unknown.	unknown.			
	$\bar{1} +$	0	81	150	1.850	620°			
	•		80	148	1.849	605°			
			<i>7</i> 9	146	1.848	590°			
			78	144	1.847	575°			
			. 77	142	1.845	560°			
			76	140	1.842	545°			
			75	138	1.838	530°			
			74	135	1.833	515°			
			73	133	1.827	501°			
	•		72	131	1.819	487°			
			71	129	1.810	473°			
			<b>7</b> 0 .	126	1.801	460°			
		- 1	69	124	1.791	447°			
	1 +	2	68	121	1.780	435°			
		1	67	118	1.769	422°			
			66	116	1.757	· '410°			
			. 65	113	1.744	400°			
		1	64	111	1.730	. 391°			
		- 1	63	108	1.715	382°			
		- 1	62	105	1.699	374°			
		ı	61	103	1.684	367°			
	•	ı	60	100	1.970	360°			
	1+	3	58.6	97	1.650	350°			
		1	50	76	1.520	290°			
		ı	40	56	1.408	260°			
	1 +	10	60	<b>3</b> 9.	1.30+	240°			
	1 +	17	20	24	1.200	224°			
	1 +	38	10	, 11	1.10-	218°			

It has been ascertained by Dr. Ure that by adding about 2½ per cent. of its weight of sulphate of potash to concentrated oil of vitriol, its specific gravity may be increased to 1.860. The only mode, therefore, of ascertaining exactly the strength of oil of vitriol is by saturating a known quantity with an alkali; and it may be assumed as sufficiently correct, that 100 grains of dry sub-carbonate of soda neutralize 92 grains of pure liquid sulphuric acid; or that 100 grains of the acid require 108, or 108.5, of the sub-carbonate for saturation.

It is sometimes of importance to the chemical artist to know the proportion, not of real acid, but of acid of commerce, in diluted sulphuric acid of different specific gravities. An approximation to the true proportion may be obtained, by increasing the numbers, indicating the real acid, one fourth. For example, acid of the specific gravity 1.200, contains according to the above table, 20 per cent of real acid; which increased one fourth, gives 25 per cent of acid of

sp. gr. 1.849. A very copious Table of the quantities of sulphuric acid of commerce in acid of different densities, constructed by Mr. Parks from actual experiment, is given in the 40th volume of the Philosophical Magazine, and in vol. ii. of his Chemical Essays, p. 144. Its length only prevents me from inserting it here. The shorter Table of Vauquelin, in the 30th volume of Nicholson's Journal, is rendered less fit for the English chemist, because the acid, employed in the experiments on which it is founded, is inferior in density to the average acid sold in this country. In taking the specific gravity of sulphuric acid, it is of importance to attend to its temperature\*, which must be examined by a thermometer, having its bulb perfectly dry. According to Dr. Ure, 100 Fahrenheit make a difference in the density of oil of vitriol of 0.005. With due attention to this, and other necessary precautions, Dr. Ure has constructed a Table, which, as it is of moderate length, and exhibits at one view the proportion not only of real or dry acid, but of liquid acid, in sulphuric acid of different specific gravities, I shall insert in the Appendix. In the memoir of which the Table forms a part, Dr. Ure has endeavoured to establish some general formulæ for calculating the proportion of oil of vitriol in dilute acid of any specific gravity, and also for finding the specific gravity corresponding to a given proportion of acidt.

(f) Sulphuric acid, by a sufficient reduction of its temperature, may be frozen; and under favourable circumstances, it assumes a regular crystalline form, a considerable degree of solidity or hardness, and a density exceeding that which it possessed in a fluid state. From the experiments of Mr. Keirt it follows that there is a certain point of specific gravity (viz. 1780 to 1000), at which the sulphuric acid most readily congeals; and when of this degree of strength it requires even a less degree of cold than is sufficient to treeze water, its congelation taking place at 45° Fahrenheit. From the specific gravity of 1786 on the one hand to 1775 on the other, it freezes at 32° Fahrenheit. It is singular that it remains congealed at a temperature higher than that originally required for freezing it. Acid, for example, which did not become solid till its temperature was reduced to 32°, remains at frozen 45°. When of the specific gravity of 1843, or as nearly as possible of that of commerce, it was found by Mr. Macnabs to freeze at - 15° Fahrenheit; but this acid, mixed with rather more than half its weight of water required for conge-

lation the temperature of - 36° Fahrenbeit.

(g) To purify sulphuric acid, it must be distilled in a glass retort, placed in the sand-bed of a reverberatory furnace. This process is a difficult one. But to those who have sufficient experience in chemical operations, the following instructions may be useful; especially as it is indispensable, in all experiments of research, to employ an acid purified by distillation.

The furnace, in which this process is conducted, should have a contrivance for supporting a sand bath within it at a proper height; and an opening in the side, for transmitting the neck of the retort.

<sup>\*</sup> See Parke's Essays, ii. 461. † Journal of Science, iv. 127. † Philosophical Transactions, lxxvii. 267. † Ibid. lxxvi. 241.

(Pl. vii. fig. 62, 63.) The retort must be coated with clay and sand over its whole body, and also over that part of the neck which is exposed to the fire. It is then to be placed, the coating being previously dry, in the sand-bath, about one half filled with sulphuric acid; and a receiver must be applied, but not luted on. The fire The first must now be lighted, and raised with extreme caution. portion that comes over, amounting to about one sixth, consists chiefly of water, and may be rejected. This is followed by the concentrated acid: and, at this period, there is great risk that the neck of the retort will be broken, by the contact of the condensed acid, which has a very high temperature, and which frequently cracks the glass, as effectually as the application of a red-hot iron. The fire must be regulated by the register door of the ash-pit, so that several seconds may elapse between the fall of the drops into the receiver. The process may be continued as long as any acid is condensed. The retorts, employed for this purpose, should be most attentively annealed.

The difficulty of rectifying sulphuric acid is much diminished, by using a retort of the capacity of from two to four quarts when a pint of the acid is employed, and by connecting its neck with the receiver by means of an adopter three or four feet long. The retort may be set over a charcoal fire, and the flame made to play gently on its bottom. No luting is to be employed, and the receiver is to be surrounded with cold water. With this arrangement, and a cautious regulation of the heat, Dr. Ure finds that sulphuric acid may be distilled without much risk, in a continuous gentle stream\*.

Sulphuric acid may be less perfectly purified by diluting it with an equal weight of water, allowing the impurities to settle, decanting the clear liquor, and evaporating it to the proper degree in a glass retort.

(h) The proportion of the elements of sulphuric acid has been investigated by several chemists. Berthollet oxygenated 17.846 parts of sulphur by nitric acid, and obtained a quantity of sulphuric acid, which gave 127.515 parts of sulphate of barytes. Hence 100 parts of sulphur would have formed 230.79 parts of real sulphuric acid (= about 292 of density 1.85); but this product falls short of what ought to have resulted. Klaproth, Richter, and Bucholz obtained results nearly agreeing with each other. Berzelius, to avoid all fallacy from the hydrogen contained in sulphur, combined it, in the first place, with lead, which, like other metals, always evolves much hydrogen, and then oxygenated the sulphuret. The following Table exhibits the proportions, deduced from different experiments, in 100 parts of real acid:

•			Oxygen.
From the experiments of	Berthollet	43.28	56,72
	Klaproth	42.20	57.80
	Berzelius	39.92	60.08
Proportions admitted by Dr.	Wollaston	40.0	60.0

If the proportions be taken at 40 sulphur and 60 oxygen, and if the acid consists, as Mr. Dalton supposes, of 1 atom of sulphur and

<sup>\*</sup> Journal of Science, iv. 116.

3 atoms of oxygen, the atom of sulphur will weigh 15; for as (60:3=) 20 is to 40 so is 7.5 to 15; and the weight of an atom of sulphuric acid will be 37.5. Mr. Dalton's numbers are 13 for the atom of sulphur, and S4 for that of sulphuric acid; the difference being

occasioned by his taking oxygen at 7, instead of 7.5.

A coincidence has been pointed out by Berzelius, which is very remarkable, and is deemed by him sufficiently general, to be admitted as a law; viz. that in any combination of two oxygenated bodies, with each other, the oxygen of the one is either a multiple or divisor of that of the other, by some simple number. Sulphuric acid, of 1850 density, affords an illustration of this principle; for it consists of 81 real acid and 19 water; and it will be found that the oxygen in the acid is, as nearly as possible, 48; and the oxygen in the water 16, so that in this case the multiple is 3, for  $16 \times 3 = 48$ . Various other examples of the same general principle will be given, in treating of metallic oxides. In all neutral compounds of sulphuric acid with alkaline, earthy or metallic bases, the acid contains a quantity of oxygen, which exceeds that in the base by the same multiple 3.

(i) Sulphuric acid is decomposed at the temperature of the atmosphere, by inflammable substances, and acquires a dark colour. The addition of a little brown sugar, or a drop of olive oil, to a portion of the acid, imparts to it a brownish hue, which in time changes to black. Hence this acid should always be kept in bottles with glass stoppers; for a small bit of straw or cork, if dropped into a considerable quantity of sulphuric acid, changes it in the manner that has

been pointed out.

(k) In high temperatures, sulphuric acid is still farther decompo-

sed by combustible bodies.

1. Hydrogen gas, brought into contact with sulphuric acid, in a state approaching ignition, decomposes it, and water and sulphurous acid are formed. This, however, is a most dangerous and difficult process, which it is not adviseable to repeat.

2. According to Gay Lussac, sulphuric acid is decomposed by heat alone, and is resolved into two parts by measure of sulphurous acid gas, and one of oxygen gas. This experiment is best performed by passing the acid through a red-hot tube of glass or porcelain.

3. Sulphur, by being boiled in sulphuric acid, partly de-oxygenates it, and converts a portion of it into sulphurous acid, which comes

over in a gaseous state.

4. Into a glass retort, put such a quantity of sulphuric acid as will fill about one fourth part of it, and add a small portion of powdered charcoal. On applying the heat of a lamp, gas will be produced very abundantly. Let this gas be conveyed by a tube fixed to the mouth of a retort, and bent in the proper manner, into an inverted jar of water; or, if it can be had, into an inverted jar of quicksilver in a mercurial apparatus. During this operation, the carbon attracts part of the oxygen of the sulphuric acid, and forms carbonic acid gas. But the sulphur is not entirely disoxygenated; and a compound is therefore formed of sulphur and oxygen, containing less oxygen than the sulphuric acid. This compound exists in the state of a gas, and its properties may next be examined. To avoid, however, the

complication which the admixture of carbonic acid with this new product introduces into the experiment, it may be proper to prepare it in a mode less objectionable, but the rationale of which cannot at present be explained. This consists in dissolving two parts, by weight, of quicksilver in one of sulphuric acid, and boiling the mass to dryness, in the bottom of a broken Florence flask. The dried mass is next to be distilled in a strong sand-heat; a glass globe being interposed between the retort and the receiving mercurial trough, to condense any sulphuric acid that may escape decomposition. (See pl. iii. fig. 31.) The gas thus obtained is termed, conformably to the principles of the new nomenclature, sulphurous acid.

#### SECTION III.

### Sulphurous Acid Gas.

SULPHUROUS acid may be formed, also, 1st, by burning sulphur at a low temperature in common air, under a glass bell; and if slips of linen cloth, dipped in a solution of potash, be exposed to the vapour, the alkali forms a combination with the sulphurous acid, which may afterwards be washed off and evaporated. The dry salt, distilled with liquid tartaric acid, gives sulphurous acid gas.

2dly. It is formed, exclusively, when sulphur is burned in dry oxygen gas. The gas, when restored to its original temperature, is found to be contracted \( \frac{1}{2} \)th or \( \frac{1}{2} \)th of its bulk; but this is probably owing to the hydrogen contained in sulphur, for there is every reason to believe that oxygen gas, by becoming sulphurous acid, is not

at all changed in volume.

Sdly. It is produced, by heating red oxide of mercury with one fourth of its weight of sulphur, in the proportion of about a cubic inch for every five grains of the oxide.

Its properties are the following:

(a) It has a pungent and suffocating smell, exactly resembling that

which arises from burning sulphur.

(b) It is more than twice as heavy as atmospherical air. One hundred cubic inches are stated by Mr. Kirwan to weigh 70.215 grains, which would make its specific gravity 2.265. By Sir H. Davy, the same volume is said to weigh 68 grains, which would give the specific gravity of 2.23. According to a calculation of Gay Lussac, founded on the proportion of its elements, its specific gravity should be 2.30314. Berzelius finds it by experiment to be 2.247\*.

(c) Monge and Clouet assert, that if the gas be exposed, at the same time, to a temperature of 31° Fahrenheit, and to great pressure,

it assumes a fluid state.

(d) It extinguishes burning bodies; and kills animals, when respired.

(e) It has the property of whitening or bleaching silk, and of giv-

ing it lustre.

(f) Of sulphurous acid, water absorbs 33 times its bulk, or one eleventh of its weight, caloric is evolved, and the solution at 68° has the specific gravity 1.0513. Mr. Dalton states the quantity absorbed

<sup>\*</sup> Ann. de Chim. et Phys. v. 178.

to be only 22 times the bulk of the water. From the solution, when recently prepared, the gas may be separated by heat, but not by congelation.

(g) The watery solution does not redden infusion of litmus, as acids in general do, but totally destroys its colour. Hence its use in bleaching several vegetable and animal products. It restores the colour of syrup of violets, which has been reddened by other acids\*.

(h) Sulphuric acid, saturated with this gas, which may be effected by passing the gas through the acid, acquires a strong smell, a yellowish brown colour, smokes when exposed to the air, and has the property of assuming a solid form, by a moderate reduction of its temperature. When distilled, the first product, which is a compound of the two acids, assumes a solid form. It has been called glacial sulphuric acid. It has however, been asserted by Vogelt, that the presence of sulphurous acid is not the cause of the glacial quality of oil of vitriol; and that, when converted to this state, by boiling in contact with sulphur, it contains no sulphurous acid. The nature of the change he has not yet fully explained.

(i) Sulphurous acid is absorbed by crystallized borax, and by means of this property, Cluzel observes, may be separated from car-

bonic acid, and some other gasest.

Sulphurous acid is again converted to the state of sulphuric by

restoring oxygen to it.

1. A mixture of oxygen and sulphuric acid gases, both perfectly dry, and standing over mercury, is not diminished by remaining in contact with each other during some months; but if a small quantity of water be added, the mixture begins to diminish, and sulphuric acid is formed. The same gases in a state of mixture, by the action of electricity, or by being driven through a red-hot porcelain tube, afford sulphuric acid. The proportions required for mutual saturation are two measures of sulphurous acid and one of oxygen gas.

2. To a portion of water saturated with sulphurous acid gas add a little oxide of manganese, a substance that contains much oxygen, loosely combined. The pungent smell of the water, and the other

characteristics of sulphurous acid, will soon disappear.

3. Sulphurous acid gas is condensed into sulphuric acid by admixture with nitrous gas, and also by oxmuriatic acid gas; but not unless the gases are in contact with water.

(k) When the temperature of sulphurous acid gas is greatly reduced, by surrounding it with a mixture of snow and muriate of

lime, it is changed into a liquid.

(1) If sulphurous acid gas and fresh muriate of tin are brought into contact over mercury, the volume of the gas is speedily diminished, sulphur is deposited, and the pro-muriate becomes a per-muriate of tin. (Accum.)

(m) It is decomposed, when submitted to the heat of ignition, in contact with certain combustible bodies. Thus, when a mixture of sulphurous acid and hydrogen gases are driven through a red-hot porcelain tube, the oxygen of the acid combines with the hydrogen,

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Nicholson's Journal, xvii. 303.

<sup>‡ 83</sup> Ann. de Chim. 259.

and forms water, and sulphur is obtained in a separate form. The sulphurous acid is decomposed, also, when transmitted over red-hot charcoal; and as appears from Gay Lussac's experiment, by potassium.

From the testimony of the same chemist we learn that 100 parts of sulphur, to become sulphurous acid, unite with 95 oxygen. The following Table shows the numbers derived from different authorities. Sulphurous acid contains per cent.

		Sulphur.			Oxygen.
According to Gay Lussac		51.30			48.70
Berzelius					
Thomson		53.0	•		47.0

The determination of Berzelius, of equal weights of its ingredients, agrees best with the specific gravity of the gas; for if 100 cubic inches weigh 68, and 100 cubic inches of oxygen 34, the remaining 34 must consist of sulphur. Its atomic constitution, according to Mr. Dalton, is 1 atom of sulphur+2 atoms of oxygen; and the weight of its atom will, therefore, be 30.

The combination of 1 atom of sulphur with 1 atom of oxygen constitutes probably the acid, which is formed in solutions of alkaline sulphurets by exposure to the atmosphere. Of this which has been called hypo-sulphurous acid, the little that is known will be found under the article sulphurets; but it has not yet been obtained in an uncombined state.

#### SECTION IV.

Combination of Sulphuric Acid with Alkalies.

ART. 1 .- Sulphate of Potash.

This salt may be formed by saturating the carbonate of potash with sulphuric acid, and crystallizing the solution. Its properties are the following:

(a) It crystallizes in small six-sided prisms, terminated by six-sided pyramids with triangular faces. Its specific gravity, according to Hassenfratz, is 2.0473.

(b) It has a bitter taste.

(c) It decrepitates when thrown on a red-hot iron, or on red-hot coals, and is volatilized by a strong heat, first running into fusion. By a low red heat it loses very little of its weight, not more than one and a half or two per cent. Indeed it does not essentially contain any water.

(d) Water, at 60° of Fahrenheit, takes up only one sixteenth of its weight; but boiling water dissolves one fifth, or by continuing

the application of heat even one fourth.

(e) The composition of this salt is determined by the quantity of sulphate of barytes, which its solution affords when decomposed by any barytic salt. From 100 parts of the ignited salt, dissolved in water, Dr. Marcet obtained 132 of sulphate of barytes, Berzelius 134.68, and Mr. R. Phillips, 136.7. Hence the composition of the salt (reckoning the acid in sulphate of barytes at 33.5 per cent.) is,

	Acid.	Base.
According to Dr. Marcet	44.22	55.78
Mr. Phillips	45.79	54.21
Bucholz	46.21	53.79
Dalton	44.70	55.30
Berard	42.76	57.24
Berzelius	45.0	55.0
Dr. Ure	45.5	5 <b>4.5</b>

If the weight of the atom of potash be 50, and that of sulphuric acid 37.5, the determination of Berard would be nearest the truth; but the proportions which would best suit the weights assigned by Mr. Dalton (42 for potash and 34 for sulphuric acid), are those approaching to 45 acid and 55 base. For though some doubt may exist as to the precise weights of the atoms of potash and sulphuric acid, it can scarcely be questioned that this salt is composed of one atom of potash united with one atom of acid. Mr. Dalton's numbers make the weight of the atom 76, and the corrected ones would increase it to 87.5.

(f) Sulphate of potash is decomposed, in high temperatures, by charcoal. Mix any quantity of the salt with one fifth of its weight of charcoal finely powdered, and expose the mixture, in a crucible, to a strong heat. The carbon will unite with the oxygen of the sulphuric acid, and will escape in the state of a gas. What remains is a compound, hereafter to be described, of sulphur and potash, or more probably of sulphur and potassium.\* No change is effected in sulphate of potash by fusion with sulphur, which sublimes unaltered.

# Bi-sulphate of Potash.

When to a saturated solution of sulphate of potash in boiling water, we add an excess of sulphuric acid, the first crystals, which are formed, contain a considerable excess of sulphuric acid, not less in the whole, according to Berthollet,‡ than 55.8 per cent. By continuing to evaporate the solution, we obtain successive quantities of crystals, which hold less and less acid in combination. Thus the second set, according to the same chemist, contain only 49.5 per cent. of acid; and he was therefore of opinion, that sulphuric acid and potash are capable of uniting in all proportions. It is much more agreeable, however, to analogy to believe, that in this, as in all other energetic combinations, the proportions are limited. The bi-sulphate or super-sulphate, it is probable, consists of one atom of base with two atoms of acid, or of 55 base + 90 acid; and its composition may be contrasted with that of the sulphate as follows:

<sup>\*</sup> Vauquelin, Ann. de Chim. et Phys. v. 31. † Ibid. p. 20. † Mémoires d' Arcueil, ii, 480. Vol. I.—M m

	•	Bi-sulphate.	•	Sulphate.
Potash	38	<b>100</b>	55	100
Sulphuric acid	62	164	45	82
	100	264	100	182

This salt has an intensely sour taste, and a powerful action on blue vegetable colours. One part is soluble in two of water at 60°, and in less than an equal weight at 212°. It is insoluble in alcohol.

## ART. 2.—Sulphate of Soda.

(a) This salt forms regular octahedral crystals, of a prismatic or cunieform figure; the two terminating pyramids of which are truncated near their basis.

(b) It has a more bitter taste than the preceding sulphate, and

melts more easily in the mouth.

(c) It swells upon a heated iron, in consequence of the loss of its water of crystallization, and a white powder is left, amounting to only about 36 parts from 100 of the original salt, or 43.2 according to Bucholz.

(d) By exposure to the atmosphere, it effloresces, and loses weight, and with so much quickness, that it is difficult to ascertain precisely its water of crystallization. Berzelius states it at

56 per cent.

(e) It is very soluble in water, three parts of which, at 60° of temperature, dissolve one of the salt; and boiling water dissolves

its own weight.

(f) Its composition is inferred from the quantity of sulphates of barytes, obtained by decomposing the solution of a known weight of this salt by any barytic salt. Bucholz, from 1000 grains of the crystallized salt (= 432 deprived of water) obtained 698 of sulphate of barytes; and Berzelius, from 5 parts of the dry salt, precipitated 8.16 of sulphate of barytes. His experiment, to have corresponded with that of Bucholz, should have given 8.12. Assuming the acid in sulphate of barytes to be 33.5 per cent, 100 parts of dry sulphate of soda (giving 161.3 of the barytic sulphate) must consist of

Mr. Dalton's numbers are 54.8 acid + .45.2 base; Dr. Wollaston's 56 + 44; Dr. Ure's 55.55 + 44.45; and those of Berzelius 55.76 + 44.24. But whichever of these numbers may be adopted,

it will be found not inconsistent with the opinion, that the salt is composed of one atom of base + one atom of acid.

The crystallized sulphate consists, calculating from the data

furnished by Berzelius, of

Acid - Water	-	-	-	-	24.64 56.
•					100.

## ART. 3.—Sulphate of Ammonia.

Sulphate of Ammonia may be composed by adding sub-carbonate of ammonia to dilute sulphuric acid; 100 parts of the compact sub-carbonate requiring, according to Dr. Ure, 88 concentrated sulphuric acid.

(a) The sulphate of ammonia forms long flattened prisms with

six sides, terminated by six-sided pyramids.

(b) It slightly attracts moisture from the air.(c) It has a cool bitter taste.

(d) Two parts of water, at 60°, take up one of the salt, and boiling water dissolves its own weight. During solution, it produces cold; and also when mingled with powdered ice, or with snow.

(e) The sublimed salt has an excess of acid; a portion of the

base being expelled by the application of heat.

(f) It contains, per cent., according to Berzelius,

•			_	100.
Water -	-	-	-	24.3
Sulph. acid	-	-	-	0011
Ammonia -	-	-	-	22.6

When dried as completely as possible without decomposing it, Dr. Ure found this salt to consist of 61 acid + 39 base, which base was itself constituted of 25.96 ammonia and 13.04 water. According to Dr. Wollaston's scale of equivalents, the numbers are 61 acid, 261 ammonia, and 131 water.\*

(g) Sulphate of ammonia liquifies, by a gentle heat, and is volatilized. If a little stronger heat be applied, it is decomposed,

and hence great care is required in drying it.

<sup>\*</sup> Thomson's Annals, x. 205.

<sup>†</sup> See Mr. Hatchett's paper in Philosophical Transactions, 1796, or Davy's Researches.

(h) The pure fixed alkalies, potash, and soda, seize the sulphuric acid, and set at liberty the alkali. Hence a strong smell of ammonia arises on the admixture of pure soda or potash with this salt.

## ART. 4.—Sulphate of Barytes.

Barytes has a powerful affinity for sulphuric acid; and the combination of these two bodies may be effected with great facility.

(a) To a solution of pure barytes, add sulphuric acid. A white

precipitate will appear, which is the sulphate of barytes.

(b) The same compound is formed, by adding sulphuric acid to carbonate of barytes, or to a solution of muriate or nitrate of barytes.

(c) The sulphate of barytes is one of the most insoluble substances, requiring for its solution 43,000 times its weight of water.

(d) Barytes has a stronger affinity than any other body for sul-

phuric acid.

(e) Owing to these properties the solutions of pure barytes, and of the nitrate and muriate of barytes, are very sensible tests of sulphuric acid, and of all its combinations. Let a single drop of sulphuric acid fall into a wine quart of pure distilled water. On adding a few drops of one of the foregoing solutions of barytes, a precipitation will ensue.

(f) Sulphate of barytes is decomposed by carbonate and subcarbonate of potash. Boil the powdered sulphate with a solution of twice or three times its weight of sub-carbonate of potash. The carbonic acid will pass to the barytes, and the sulphuric to the

potash.

Some curious facts respecting this decomposition have been ascertained by Mr. Richard Phillips.\* When sulphate of barytes is boiled, for two hours, in contact with precisely its equivalent quantity of sub-carbonate of potash, (that is, with the quantity which ought to produce entire decomposition), only one fourth of the sulphate of barytes is converted into carbonate. Reversing the process, and boiling together equivalent quantities of carbonate of barytes and sulphate of potash (the mutual decomposition of which could not have been expected from the established order of affinities) it was found that, out of 85 parts of carbonate of barytes, 57 had been changed into sulphate. It is obvious, therefore, that the entire decomposition of sulphate of barytes by carbonate of potash can never be expected, so long as the carbonate of barytes, formed by the mutual action of these two salts, remains in contact with the sulphate of potash generated at the same time; for this will re-convert the carbonate of barytes into sulphate. Nor

<sup>\*</sup> Journal of Science, &c. i. 80.

will any quantity of carbonate of potash, that can be employed, be adequate to the entire decomposition of the sulphate of barytes.

(g) By this process carbonate of barytes may, however, be procured in sufficient quantity for the purpose of preparing the pure earth, and its various salts, when the native carbonate cannot be had in sufficient abundance. The sulphate is found, in considerable masses, accompanying lead ore, in Derbyshire and other parts of England, where it is known by the names of cawk, ponderous When applied to the purpose of obtaining the carbospar, &c. nate of barytes, it is to be finely powdered, mixed with three or four times its weight of sub-carbonate of potash, and boiled with a proper quantity of water for a considerable time, in an iron kettle, stirring it, and breaking down the hard lumps, into which it is apt to run, by an iron pestle. It is then to be washed with boiling water, as long as this acquires any taste. On the addition of dilute muriatic acid, a violent effervescence will ensue, and a considerable portion of the earth, probably along with some metals, will be dissolved. To the saturated solution, add solution of pure ammonia, or, in preference, a solution of pure barytes in water, as long as it disturbs the transparency of the liquor. This will throw down any metals that may be present; and the barytes may afterwards be precipitated in the state of a carbonate, by a solution of carbonate of potash. Let the precipitated earth be well washed with distilled water; and if the pure barytes is to be obtained from it, let it be treated as directed, chap. x.

(h) Sulphate of barytes is also decomposed when ignited with powdered charcoal, which abstracts the oxygen of the sulphuric acid, and leaves a combination of sulphur and barytes. From this, the barytes may be removed by muriatic acid, as already directed, and the muriatic solution be decomposed by carbonate of potash.

(i) The sulphate of barytes, when decomposed by charcoal, affords one variety of solar phosphorus. This phosphorus has been called, from the place where the sulphate is found from which it was first prepared, the Bolognian phosphorus. The native sulphate, powdered after being ignited, and finely sifted, is to be formed into a paste with mucilage of gum arabic, and divided into cylinders or pieces of one fourth of an inch in thickness. These after being dried in a moderate heat, are to be exposed to the temperature of a wind furnace, placed in the midst of the charcoal. When the fuel is half consumed, it must be replenished, and suffered to burn out. The pieces will be found, retaining their original shapes, among the ashes, from which they may be separated by the blast of a pair of bellows. They must be preserved in a well-stopped phial.

This phosphorus, after being exposed a few minutes to the sun's rays, shines in the dark sufficiently to render visible the dial of a watch. This property is lost by repeated use, in consequence of the oxygenation of the sulphur; but may be restored by a second

calcination.

(k) Sulphate of barytes, when artificially formed and calcined, contains in one hundred parts,

		Base.	Acid:
According to Klaproth -	-	<b>66.55</b>	<b>33.45</b>
Mr. A. Aikin*	-	<b>66.</b> 04	<b>36.9</b> 6
Mr. J. Thomsont		66 <b>.</b> 96	<b>3</b> 3.04
Berthollett -	••	66:50	33:50 <sup>,</sup>
Berzelius -	-	65.69	34.31

The determination of Berthollet, being nearly a mean of three; may be considered as sufficiently accurate: Dr. Wollaston assumes: 66 parts of base and 34 of acid; as expressing most correctly its composition. The native sulphate, according to Klaproth, is composed of one third acid and two-thirds base. Its atomic constitution is one atom of base and one of acid:

## ART. 5 .- Sulphate of Strontites.

I. This salt resembles, very nearly, the sulphate of barytes. It may be formed in a similar manner, by pouring the solution of pure strontites into diluted sulphuric acid, or into the solution of an alkaline sulphate; for it has a stronger affinity than any of the alkalies for sulphuric acid. It is soluble in 3840 parts of boiling water.

II. The sulphate of strontites is also found native in considerable quantities; chiefly at Aust Passage, and at other places in the neighbourhood of Bristol. As the native carbonate is now becoming scarce, this compound may be advantageously employed for procuring artificial carbonate of strontites. This process is precisely similar to that already described for decomposing the sulphate of barites. (Art. 4. g.)

According to a considerable majority of the chemists who have

analyzed it, it consists of

Acid	-	-	_	42	_	100
Strontites		-	-	58	-	138
				100		238

The accuracy of these numbers is admitted by Dr. Wollaston. But Vauquelin has stated, that it is composed of 46 acid and 54 base, and Stromeyer of 43 acid and 57 base.

# ART. 6.—Sulphate of Lime.

I. The sulphate of lime is formed, by adding to the carbonate a sufficient quantity of sulphuric acid; and by gently calcining the

<sup>\*</sup> Nicholson's Journal, xxii. 301. † Mémoires d'Arcueil, ii.

Contributions, is 377.

<sup>†</sup> Nicholson's Journal, xxiii. 174. § 79 Annales de Chimie, 138.

residue, to expel the redundancy of the latter acid. It is also found native, in great abundance, under the names of gypsum, plaster of Paris, &c.

II. It has the following properties:1. It is insipid and free from smell.

2. It is difficultly soluble, requiring 500 times its weight of cold

water, or 450 of hot water.

3. It is fusible by a moderate heat. When sulphate of lime, which has been dried at 160° Fahrenheit, is exposed to a low redheat, it loses 22 (according to Berzelius, and Bucholz 21) per cent. of its weight, consisting entirely of water. After calcination, it

absorbs water rapidly, and forms a good cement.

4. It is decomposed by carbonates of alkali, a double exchange of principles ensuing. Hence the milkiness which ensues on adding carbonate of potash to many spring waters; the carbonate of lime, which is generated, being less soluble than the sulphate. Hence, also, hard waters, which always contain sulphate of lime in solution, curdle soap, the alkali of which is detached by the sulphuric acid, and the oil is set at liberty.

5. It is decomposed by ignition with charcoal, which separates the oxygen of the sulphuric acid, and leaves a combination of lime

with sulphur.

By dissolving 100 grains of calcined sulphate of lime in boiling distilled water, and adding muriate of barytes, I obtained a precipitate, which, when well washed, dried, and calcined in a low red-heat, weighed 175.9. Hence 100 parts of calcined sulphate of lime must contain very nearly

				Acid.	Base.
According to the above expe	rimen	t	-	59	41
. Thompson and	Berz	elius		<b>58</b>	42
Klaproth	_	-	-	57.63	42.37
———— Dalton		-	-	<b>58.60</b>	41.40

It consists, therefore, of an atom of lime united with an atom of acid.

# ART. 7.—Sulphate of Magnesia.

I. When highly concentrated sulphuric acid is suddenly added to fresh prepared and pure magnesia, very great heat and vapour are excited, and are accompanied frequently with an extrication of light. This appearance was first observed by Westrumb.

II. If the carbonate of magnesia be added to diluted sulphuric acid, the carbonic acid is expelled, and a solution of sulphate of magnesia is formed, which crystallizes on cooling. Crystals of sulphate of magnesia may also be procured in the shops, under the name of Epsom salt.

III. These crystals have the following properties:

1. They have the form of small quadrangular prisms, surmounted by quadrangular pyramids with dihedral summits. They undergo no change by exposure to the atmosphere.

2. At the temperature of 60°, this salt is soluble in an equal weight of cold water, and in three-fourths its weight of boiling water, which thus receives an addition of one fourth of its bulk.

3. When exposed to a low red-heat, it undergoes the watery fusion, but is not volatilized. It loses, however, about one half its weight, which is water of crystallization, and, according to Berze-

lius, a very minute portion of acid escapes.

4. One hundred grains of sulphate of magnesia, deprived, by calcination in a low red-heat, of its water of crystallization, afforded me 200 grains of sulphate of barytes when precipitated by the muriate of the latter earth. Hence 100 grains of dry sulphate of magnesia are composed of 67 acid and 33 magnesia, and the crystallized salt, supposing it to contain half its weight of water, will consist in 100 parts of

50 water, 33.5 sulphuric acid, 16.5 magnesia.

Berzelius, from 100 grains of desiccated sulphate of magnesia, ebtained 194.3 of sulphate of barytes. Hence the dry salt consists of 65.1 acid and 34.9 earth, and its atomic constitution is

one atom of earth + one atom of acid.

5. Its solution is precipitated by carbonates of potash and of soda; but not by carbonate of ammonia, unless heat is applied. The carbonate of magnesia of the shops is prepared by mixing together concentrated and hot solutions of carbonate of potash and sulphate of magnesia. The sulphate of potash, thus formed, is removed by copious washing with water, and the carbonate of magnesia is then dried. The proportions employed are filtered solutions of 4 parts of the crystallized sulphate, and 3 of the sub-carbonate. One hundred parts of the desiccated sulphate give about 71 of subcarbonate of magnesia, or about 31.6 of the pure earth.

6. When a dilute solution of carbonate of soda is mixed with a dilute solution of sulphate of magnesia, and the sub-carbonate which is formed, if any, is separated by filtration, crystals of carbonate of magnesia, after some time, shoot in the liquid, containing a larger proportion of water, but no more carbonic acid than the common carbonate, see chap. x. sect. 4. When solution of pure ammonia is added to that of sulphate of magnesia, part of the earth is precipitated. The rest remains in solution, and, by evaporation, a triple salt is formed, consisting of sulphuric acid, magnesia, and ammonia, and called ammoniaco-magnesian sulphate.

A compound Sulphate of Magnesia and Soda has been described by Dr. Murray, in a note to his paper on the Analysis of Sea Water.\* It crystallizes in rhombs truncated on the angles and edges;

is soluble in rather more than three times its weight of water at 60° Fahrenheit; is permanent in the air; and does not fuse, but decrepitates on applying heat. It is composed of

Sulphate of magnesia Sulphate of soda -	-	-	-	32 39
Water of crystallization	-	-	' <b>-</b>	29
				100

## ART. 8.—Sulphate of Alumine and Alum.

The properties of this salt may be exhibited by those of the common alum of commerce; though, as will afterwards appear, alum is not merely a combination of this earth with sulphuric acid; but is a triple salt, composed either of sulphuric acid, alumine, and potash; or of sulphuric acid, alumine, and ammonia. It has the following characters:

(a) It has a sweetish astringent taste. Its specific gravity is

1.71.

(b) It dissolves in water, five parts of which, at 60°, take up one of the salt, but hot water dissolves about three fourths of its weight.

(c) This solution reddens vegetable blue colours; which proves

the acid to be in excess.

(d) When mixed with a solution of carbonate of potash, an effervescence is produced by the uncombined acid, which also prevents the first portions of alkali, that are added to a solution of sulphate of alumine, from occasioning any precipitate.

(e) On a farther addition of alkali, the alumine is precipitated.
(f) Sulphate of alumine, when heated, swells up, loses its regular form, and becomes a dry spongy mass: but, according to Vau-

quelin,\* the whole of its acid cannot be expelled by heat.

(g) The combination of sulphuric acid with alumine is incapable of crystallizing without an admixture of sulphate of potash, which forms a constituent of all the alum of commerce. According to Vauquelin, 100 parts consist of 49 dry sulphate of alumine, 7 sulphate of potash, and 44 water. Or 100 grains are composed of

			100.00†		100±		99.90§
Water		-	48.58	-	47	-	<b>46.</b> -
Potash			10.40	-	9 .	-	9.81
Alumine		-	10.50	-	12	-	10.86
Acid	<b>-</b> .	-	30.52	•	33	-	34.23

<sup>\*</sup> Ann. de Chim. xxxvii. 91. † Vanquelin. † Dalton Berzelius. In this there is a deficiency of 0.1 per cent. Vol. I.—N n

The acid, in Vauquelin's estimate, is evidently rated too low; for alum, when precipitated by muriate of barytes, gives, as nearly as possible, an equal weight of sulphate of barytes, 100 grains of which contain 33.5 of sulphuric acid, the quantity, therefore, present in 100 parts of alum. According to Berzelius, alum is composed of

Sulphate	of alumi	ne	-	-	36.85
	potasł		-	•	18.15
Water	•	-	•	-	45.
					-
			•		100

The oxygen of the potash being represented by 1, Berzelius finds that the oxygen of the alumine will be as 3; that of the sulphuric acid as 12; and that of the water as 24. The salt consists, according to Mr. Dalton, of one atom of sulphate of potash, four atoms of sulphate of alumine, and 30 atoms of water. The alumine, he contends, does not exist in the state of super-sulphate, but of a saturated sulphate, a salt composed of

Alumine Acid	-	-	-	29.934 70.066
				100.

A neutral sulphate of alumine was obtained by Berzelius, by the following process. He decomposed alum by ammonia; washed the precipitate, and redissolved it in sulphuric acid. To the liquor, after evaporation, he added alcohol, which threw down a sulphate nearly neutral, and rendered perfectly so, by being washed with farther portions of alcohol. Gay Lussac has also given the following process; communicated to him by Descotils, for preparing a pure sulphate of alumine. On alum with base of ammonia, boil nitro-muriatic acid, till all the ammonia is destroyed, and evaporate to dryness to expell all the nitric and muriatic acids. The ammonia is decomposed by the chlorine, which results from the mutual action of those two acids, and the alumine remains in combination with sulphuric acid only. The saturated solution of this salt in water is an excellent test to discover potash, for a drop or two added to a solution of that alkali, or of any of its salts, immediately causes a precipitation of alum.\*

(h) Alum is decomposed by charcoal, which combines with the oxygen of the sulphuric acid, and leaves the sulphur attached to the alumine. A combination of alumine, sulphur, and charcoal, forms the pyrophorus of Homberg. To prepare this, equal parts of powdered alum and brown sugar are melted over the fire, and are kept stirring till reduced to dryness. The mixture, when cold, is to be finely powdered, and introduced into a common phial, coated with clay, to which a glass tube, open at each end, is to

<sup>\*</sup> Ann. de Chim. et Phys. vi. 201.

be luted, to allow the escape of the gases that are produced. The phial must then be set in the fire, surrounded by sand, in a crucible. Gas will issue from the open end of the tube, and may be inflamed by a lighted paper. When this ceases to escape, the crucible may be removed from the fire, and a little moist clay pressed down upon the open end of the tube, to prevent the access of air to the contents of the phial. When cold, the tube may be removed, and a cork substituted in its place. The principal difficulty in the process, is to stop it precisely at the period, when the pyrophorus is formed; for if the heat be continued longer, the preparation will be spoiled.

The pyrophorus thus formed is a black and light powder, which instantly takes fire when poured out of the bottle into the air, and inflames suddenly in oxygen gas. Sulphate of potash appears to be essential to its production, and hence the sulphuret of potash is a necessary ingredient. From the discoveries of Sir H. Davy, it appears not improbable that this pyrophorus may contain sulphuret of potassium. The principal part of the phenomena, however, is owing to the combustion of an extremely light and finely

divided charcoal.

# ART. 9.—Sulphate of Glucine.

Glucine combines readily with sulphuric acid, both in its pure and carbonated state. The resulting salt is extremely soluble; insomuch that, when evaporated, it assumes the form of a syrup, without crystallizing. Its taste is sweet, and rather astringent. It is decomposed entirely in a high temperature, the earth being left in a state of purity. It is also destroyed by ignition with charcoal. It does not yield its earthy ingredient to any of the acids; but is decomposed by all the alkalies and earths, allumine excepted.

# ART. 10.—Sulphate of Zircon.

To effect the combination of zircon with any acid, this earth should be fresh precipitated; for, after being dried, it enters with

difficulty into union.

The salt, resulting from the union of sulphuric acid with zircon, is white, insoluble, and without taste. It is decomposed by a high temperature, which expels the acid, and leaves the zircon pure. It is not changed by other acids, but yields its sulphuric acid to the alkalies, and to most of the earths.

# ART. 11 .- Sulphate of Yttria.

Sulphuric acid readily dissolves yttria, and caloric is evolved during the process. As the solution goes on, the sulphate crystal-

lizes in small brilliant grains, which have a sweetish taste, but less decidedly than the sulphate of glucine. Their colour is a light amethyst red. They require 30 parts of water, of the temperature of 60°, for solution, and give up their acid when exposed to a high temperature. They are decomposed by oxalic acid, prussiate of potash, infusion of galls, and phosphate of soda.

#### SECTION V.

## Sulphites.

I. The combination of sulphurous acid with alkaline and earthy bases, may be effected by passing the gas, as it proceeds from the materials (sect. 2, h,) through the base, dissolved or diffused in An intermediate vessel may be placed, as represented, water. fig. 30 and 31, to condense any sulphuric acid that may pass over; and the solution of the alkali or earth may be contained in a bottle with two necks. Pure potash, soda, or ammonia, are readily kept in solution: but barytes or strontites must be dissolved in boiling water; and the bottle containing them must be surrounded with hot water, while the gas is transmitted through the solution. The solution, when saturated with gas, may be evaporated; and this is best done in an alembic, covered with its capital, because the salts of this class are changed by the action of the atmosphere.

II. The sulphites have no peculiarly interesting properties, that can entitle them to minute and specific description, in a work devoted solely to the students of chemical science. I shall enumerate, therefore, only the principal ones; and refer, for farther information, to the 2d and 24th volumes of the Annales de Chimie, and to Dr. Thomson's memoir in Nicholson's Journal, vi. 94.

Their general qualities are the following:

1. They have a disagreeable taste and smell, resembling the

fumes of burning sulphur.

2. When heated, they emit sulphurous acid and water, and then sulphur, which, on the application of an inflamed substance, takes fire, and burns violently.

3. Exposed to the atmosphere, in a state of solution, or moistened with water, they absorb oxygen, and are slowly converted into sulphates, without undergoing any change in their state of neutralization.

4. When added to nitric acid, red fumes arise, and the salts become sulphates. Oxy-muriatic acid produces the same effect. Concentrated sulphuric acid expels sulphurous acid gas, which

may be collected over mercury.

5. When sulphureted hydrogen gas is passed through a solution of the sulphites, they combine with an additional quantity of sulphur, and form sulphureted sulphites. These compounds are regarded by Gay Lussac, not as sulphites holding sulphur in solution, but as resulting from the union of a base with a distinct acid, to which he has given the name of the per-sulphurous or hypo-sulphurous acid,\* and to its compounds that of hypo-sulphites. When sulphur is boiled with the sulphites in solution, sulphur is taken up, and sulphurous acid escapes.

6. When perfectly pure, sulphites are not precipitated by a solution of pure barytes or strontites, or by any of the salts with base of either of those earths. If a precipitation ensue, it indi-

cates the presence of a portion of sulphate.

SULPHITE OF POTASH crystallizes in the form of lengthened rhomboidal plates; or of needles, which have sometimes a slight yellowish tinge. It has a pungent and sulphurous taste, and is soluble in an equal weight of cold, or in less than an equal weight of boiling water. At the temperature of 300° Fahrenheit, it loses only about 2 per cent; but when more strongly heated, the salt is decomposed, and sustains a loss of about 22 per cent, of which 15 are sulphurous acid, 5 sulphur, and 2 water. When thrown into a red-hot crucible, a blue flame arises from it, and its weight is diminished in the proportion which has just been stated. When this solution is exposed to the air, the salt slowly attracts oxygen, and is converted into sulphate of potash. This change goes on more rapidly in oxygen gas; or when it is mixed with any substance holding oxygen in loose combination, as nitric or oxymuriatic acid. It contains, in 100 parts, from Dr. Thomson's experiments,

> 43.5 acid 54.5 potash 2 water

100

SULPHITE OF SODA forms compressed tetrahedral prisms with dihedral summits. It requires for solution less than its own weight of boiling water, or four times its weight of cold water. It effloresces in the air, but much less perfectly than the sulphate of soda. It is composed, according to Dr. Thomson, of

31 acid 18 soda 51 water -----

SULPHITE OF AMMONIA crystallizes in hexahedral prisms terminated by pyramids with the same number of sides, or in rhomboidal prisms with trihedral summits. It is soluble in an equal weight of cold water, or in less than an equal weight of boiling water.

<sup>\*</sup> Ann. de Chim. et Phys. vi. 323, note. † Gay Lussac, 85 Ann. de Chim. 199.

It deliquiates in the atmosphere, and absorbing oxygen is changed

into sulphate of ammonia, which becomes dry.

SULPHITE OF BARYTES, like the salt formed by uniting the same base with salphuric acid, is almost insoluble. When united with an excess of sulphurous acid, however (which may be done by dissolving the white powder, that is first formed, in liquid sulphurous acid), it forms a crystallizable salt, still of sparing solubility, consisting of

Base	-	-	69.74
Acid	-	-	28.84
Water	-	-	1.42
			100

The solution of this salt may be advantageously used to purify the solution of any sulphite from sulphuric acid, which it precipitates in the state of an insoluble sulphate of barytes.

SULPRITE OF LIME is also insoluble, but may be crystallized by being first dissolved in liquid sulphurous acid. In this state it re-

quires 800 parts of water for solution.

SULPHITE OF MAGNESIA differs from the sulphate of this earth in being vastly less soluble in water, of which it requires 20 parts at the common temperature. Hot water takes up a farther portion, which is deposited on cooling.

SULPHITE OF ALUMINE is not crystallizable, but has the form of a white soft powder, insoluble in water, but soluble in an excess

of acid. It consists, according to Dr. Thomson, of

32 acid 44 alumine 24 water

100

## SECTION VI.

Binary Compounds of Sulphur.—1st, With Alkalies.—2d, With Hydrogen.

# ART. 1.—Sulphurets.

I. The combination of sulphur with the fixed alkalies and earths may be effected by fusing together, in a covered crucible, at a degree of heat below redness, equal parts of sulphur and of the alkali or earth intended to be united with it. The sulphurets of potash and soda may, also, be obtained by a similar treatment of six parts of sulphur with eight of either of the sub-carbonates of those alkalies, previously dried as completely as possible. The com-

pound may be poured, while in fusion, upon a smooth stone, and, when cold, preserved in a well closed phial. Its colour is a brownish red or liver colour, from which property has been derived the generic name, formerly in use, of hepar or liver of sulphur.

It was contended by Vauquelin that, during the formation of sulphurets by fusion, a considerable quantity of sulphureted hydrogen gas is evolved, and that sulphuric acid is also produced, which, uniting with the alkaline base, composes a sulphate. It has been shown, however, by Gay Lussac, that the formation of sulphuric acid takes place only at high temperatures, and that a sulphuret, which has been prepared at a degree of heat barely sufficient for the purpose, when dissolved in water, gives no trace of sulphuric acid, but abounds with hypo-sulphurous acid. This acid must, however have been generated during the act of solution, by the decomposition of water, for it is incapable of being formed, or even of existing, at high temperatures.

A pure sulphuret of potash or soda cannot be formed in the humid way, for the decomposition of the water gives rise to other products, which, also, exist in the solution. According to Vauquelin, the sulphuret of lime is an exception to this rule, and may be formed by boiling lime and sulphur with a sufficient quantity

of water.

It has been doubted whether, in the production of alkaline and earthy sulphurets, the base preserves the state of an oxide after combination with sulphur, or whether it be de-oxydized, and thus produce a sulphuret with the metallic base of the respective alkali or earth. The oxides of the common metals, it is well known; abandon their oxygen, when fused with sulphur, and afford true metallic sulphurets. Gay Lussac has, however, proved that, at a moderate temperature, the alkalies unite, as such, with sulphur, and that compounds are formed which are true sulphureted oxides.\*

To prepare sulphuret of ammonia, a mixture of one part of dry quicklime, one of muriate of ammonia, and half a part of sulphur, may be distilled from a glass retort by a gentle heat. The product is a liquid of a brownish yellow colour, and an oily consistence, which emits copiously white and offensive fumes.

Sulphuret of lime, when intended for the purpose of Canton's phosphorus, is best prepared, by placing in a crucible, alternate strata of calcined and pounded oyster-shells and sulphur; exposing them to a moderate heat; and then confining them in a bottle with a ground stopper. Or, according to the original directions of Canton, three parts of oyster-shells, calcined for an hour and pulverized, are to be mixed with one of sulphur, and rammed tightly into a crucible, which is to be kept red-hot for about an hour. The compound, when cold, has the properties already assigned to the Bolognian phosphorus.

II. Sulphurets have the following properties:

<sup>\* 6</sup> Ann. de Chim. et Phys. 325.

(a) In a moist state they emit an offensive smell, and have a disagreeable taste.

(b) They change to green the colour of violets, in the same

manner as uncombined alkalies.

(c) They blacken the skin, silk, and other animal substances.

(d) They are decomposed by all acids. Into a Nooth's machine put a weak solution of sulphuret of alkali, and pass through it streams of carbonic acid gas. In the course of a few days, the sulphur will be precipitated, and a carbonate of alkali will be obtained. This decomposition ensues, instantly, on adding, to a solution of sulphuret of potash, any of the stronger acids, as the sulphuric, nitric, or muriatic; and we obtain a compound of the alkali with the respective acid employed.

(e) The solutions of sulphurets absorb oxygen gas, and abandon part of their sulphur. This may be shown by the experiments already described (chap. v.) If the change thus effected be examined, it will be found that the oxygen has combined with the sulphur, and formed sulphurous acid, which, uniting with the alkali, has composed the sulphite of potash. To this sulphite, a portion of the liberated sulphur unites itself, forming a sulphu-

reted sulphite.

(f) If dilute muriatic acid be poured on the solution of sulphuret of potash or soda, a violent effervescence will ensue, and a very offensive gas be disengaged. This gas may be collected over water. It is termed sulphureted hydrogen gas. From the experiments of Vauquelin, it appears to be merely disengaged, and not formed by the action of the acid. The following Table shows the composition of a few of the sulphurets, as determined by Vauquelin. No sulphuret of magnesia has yet been proved to exist.

					100 Base
			Base.	Sulphur.	take Sulphur.
Sulphuret of Potash	-	-	47.3	- 52.7	111.5
				- 62.	163.
Barytes	-	-	65.5	- 34.5	52.5
				- 63.	170.

The quantities of sulphur, which combine with the alkalies and earths, have been ascertained by the same chemist to be proportional to the quantities of oxygen, with which their respective metallic bases are united. But the sulphurets contain more sulphur than is necessary to form the quantity of sulphuric acid, equivalent to the saturation of their bases.

# ART. 2.—Sulphureted Hydrogen Gas.

This gas may be procured:

1. By the action of diluted sulphuric acid on sulphuret of iron, prepared in the following manner. A bar of iron is to be heated to a white or welding heat in a smith's forge, and, in this state, is to be ruobed with a roll of sulphur. The metal and sulphur unite,

and form a liquid compound, which falls down in drops. These soon congeal; and the compound must be preserved in a well closed phial.

2. The sulphuret, prepared by melting iron filings with sulphur in a crucible, does not answer the purpose equally well, because the gas, which it affords, is mixed with a good deal of hydrogen gas. So, also, is the sulphureted hydrogen produced by heating

sulphur in hydrogen gas.

3. Gay Lussac prepares sulphuret of iron by introducing into a matrass two parts by weight of iron filings, and one of flowers of sulphur. To these, water is added in sufficient quantity to give a thickish consistence; and the matrass is heated a little, to favour the combination, which is indicated by a copious disengagement of heat, and by the whole mass assuming a black colour. From this compound, sulphuric acid, diluted with four times its volume of water, separates sulphureted hydrogen in great abundance. It is better to prepare the compound when wanted, than to keep it ready made, because, unless very carefully preserved from contact with the air, it becomes less fit for the purpose of affording gas.\*

4. The sulphuret of potash, if prepared by boiling flowers of sulphur with liquid potash, quite free from carbonic acid, gives pure sulphureted hydrogen, when acted upon by diluted sulphuric

or muriatic acid.

II. Its properties are the following:

(a) Its smell is extremely offensive, resembling that of putre-

fying eggs.

(b) It is inflammable, and burns either silently or with an explosion, according as it is previously mixed, or not, with oxygen gas or atmospheric air. During this combustion, water results from the union of the hydrogen with the oxygen, and sulphuric and sulphurous acids from that of the oxygen and sulphur. Two measures require three of oxygen gas, one measure of which saturates the hydrogen, and two the sulphur.

When three parts of sulphureted hydrogen are mingled with two of nitrous gas, the mixture, on being inflamed, burns with a

yellowish green flame.

(c) It tarnishes silver, mercury, and other polished metals, and

instantly blackens white paint.

(d) It is absorbed by water, which takes up its own bulk, or according to Saussure twice and a half, or Gay Lussac, three times, its bulk of the gas; but in order to obtain so considerable an absorption, the gas, submitted to experiment, should be perfectly pure. Water thus saturated acquires the peculiar smell of the gas. It is this gas which gives to the Harrogate, and some other natural waters, their disagreeable odour. Liquid muriatic acid absorbs at least three times its volume; and sulphuric acid, diluted with an equal weight of water, once and a half its volume.

<sup>\*</sup> Ann. de Chim. et Phys. vii. 314.

(e) Water, saturated with this gas, reddens the infusion of violets, in this respect producing the effect of an acid. From this and other properties, some of the German chemists have proposed for it the name of hydrothionic acid; and Gay Lussac has given it the very objectionable name of hydro-sulphuric acid, a term which would be much more properly applied to liquid sulphuric acid.

(f) Water impregnated with sulphureted hydrogen, when exposed to the atmosphere, becomes covered with a pellicle of sulphur. Sulphur is even deposited when the water is kept in well-

closed bottles.

(g) On the addition of a few drops of nitric or nitrous acid to the watery solution, sulphur is instantly precipitated. In this case the oxygen of the acid combines with the hydrogen of the gas, and the sulphur is separated. The gas itself, also, is decomposed when transmitted through sulphuric, nitric, or arsenic acids.\*

(h) This gas, as will afterwards appear, is decomposed by mixture with oxy-muriatic acid gas; and sulphur is precipitated. Vogel obtained, also, a liquid, analogous to the sulphureted muriatic

acid of Dr. Thomson.

(i) It is decomposed also when kept in a state of mixture with atmospheric air, the oxygen of which combines with the hydrogen, and forms water, while the sulphur is precipitated.

(k) A succession of electric explosions throws down sulphur

from it, and the volume of the gas remains unaltered.

(1) When six measures of sulphureted hydrogen gas and five measures of sulphurous acid gas are mingled together, the hydrogen of the former unites with the oxygen of the latter, and the sulphur of both is precipitated. But five measures of sulphurous acid contain twice the oxygen necessary for saturating six measures of sulphureted hydrogen. Hence it is probable, that the sulphur is separated in the state of an oxide.

(m) It is decomposed when passed over ignited charcoal, and

is converted into carbureted hydrogen gas.

(n) Sulphureted hydrogen, both in the state of a gas and of watery impregnation, precipitates all metallic solutions, excepting those of iron, nickel, cobalt, manganese, titanium, and molybdena.

(o) It is copiously absorbed by alkalies, and by all the earths, excepting alumine and zircon. These alkaline and earthy com-

binations are termed hydro-sulphurets.

(p) When potassium or sodium is made to act on sulphureted hydrogen gas, a brilliant combustion takes place; a quantity of hydrogen gas is evolved, precisely equivalent to that which the metal would have separated from water; the metal loses its lustre, and becomes grayish, or amber coloured, or reddish; and by the action of diluted muriatic acid, the whole of the sulphureted hydrogen, is recovered. This experiment proves, that sulphureted hydrogen, and consequently sulphur, contain no oxygen; for, in that case, the potassium would not, after being acted on by the gas, evolve the original quantity of sulphureted hydrogen. All that appears

<sup>\*</sup> Journal of Science, &c. ii. 152.

to take place is, the combination of the metal with sulphur, and the formation of a sulphuret of potassium or sodium, which disengages from water exactly as much hydrogen, as would have been evolved by the metal in its separate state. The results of Sir H. Davy, which are somewhat different, are satisfactorily ex-

plained by Gay Lussac and Thenard.\*.

(q) The specific gravity of sulphureted hydrogen gas has been variously stated. Mr. Kirwan found 100 cubic inches, at 60° Fahrenheit, and 30 inches barometer, to weigh 34.286 grains, which makes its specific gravity 1.124. Sir H. Davy states the weight of the same quantity at 36.5 grains, and its specific gravity, therefore, at 1.180. Gay Lussac and Thenard determined its specific gravity to be 1.1912 by experiment, or 1.1768 by calculation; and 100 cubic inches should weigh 36.33 grains, according to the first of these two numbers.

(r) Admitting the accuracy of Sir H. Davy's statement of its specific gravity, and also that 100 cubic inches of the gas contain exactly the same volume of hydrogen (≠ 2.27 grains), then 36.5 grains of sulphureted hydrogen will contain 2.27 grains of hydrogen.

gen; and 100 grains will consist of

Sulphur - 93.8 Hydrogen - 6.2 100.

From these data, which agree very nearly with those of Berzelius,† the weight of the atom of sulphur may be stated at 15; for as 6.2 to 93.8 so is 1 to 15 very nearly. The weight of this atom, therefore, turns out to be the same, whether investigated by its combinations with oxygen or with hydrogen.

# ART. 3.—Hydro-Sulphurets.

In its union with alkaline and earthy bases, sulphureted hydrogen seems to perform, in a great measure, the functions of an acid; and presents, therefore, an important exception to the doctrine of acidification proposed by Lavoisier; for, in this instance, a body, which contains no oxygen, possesses some of the most important characters of an acid, viz. the property of changing vegetable blues to red, and of uniting with alkalies.

I. The hydro-sulphurets may be formed, by transmitting sulphureted hydrogen gas, as it issues from the materials that afford it, through a solution of the alkaline or earthy base. Or the base, when insoluble, must be kept suspended in water by mechanical

agitation.

II. The hydro-sulphurets have several qualities common to the

whole genus.

1. They are all soluble in water, and the recent solution is colourless. By exposure to the air however, it first becomes green,

<sup>\*</sup> Recherches, i. 202.

<sup>† 81</sup> Ann. de Chim. 26.

or greenish yellow, and deposits sulphur on the sides of the vessel. The glass bottle, containing the solution, becomes black on its inner surface, in consequence of the combination of sulphur with the oxide of lead contained in the glass.

2. The solution of hydro-sulphuret of magnesia is decomposed by heat; that of lime nearly so; but those of potash and soda, though rendered much more alkaline by heat, still contain a large

proportion of sulphureted hydrogen.

3. After long exposure to the atmosphere, the solution entirely loses its colour, and again becomes perfectly limpid. When examined, it is found to consist of a combination of sulphuric acid with the peculiar base of the hydro-sulphuret. This is owing to the absorption of oxygen, which all hydro-sulphurets take from the atmosphere; the formation of a sulphite; and the conversion of this, by farther oxygenation, into a sulphate. Hence, when confined in contact with a limited quantity of atmospherical air, hydro-sulphurets effect a diminution of volume; and may be employed to ascertain its proportion of oxygen. They entirely absorb pure oxygen gas.

4. When a hydro-sulphuret, fully charged with gas, is heated with sulphur, a strong effervescence ensues; much of the sulphur is dissolved; and sulphureted hydrogen escapes. If the hydrosulphuret is not fully saturated, sulphur is still dissolved, but with-

out any escape of sulphureted hydrogen.

5. When an acid is poured on any of the hydro-sulphurets, the sulphureted hydrogen gas is disengaged and no sulphur is deposited. This non-precipitation of sulphur distinguishes hydro-sulphurets, both from sulphurets and hydrogureted sulphurets. The acid employed should be one which strongly retains its oxygen, such as the sulphuric or muriatic; otherwise it will be decomposed. A hydro-sulphuret, which has been a few days exposed to the air, yields, by this treatment, sulphurous acid gas, along with sulphureted hydrogen.

6. The solutions of hydro-sulphurets precipitate all metallic solutions. They also precipitate alumine and zircon from their

solutions, but no other earths.

7. The hydro-sulphurets are, for the most part, susceptible of a

regularly crystallized form.

Hydro-sulphuret of potash forms large transparent crystals not unlike in size those of sulphate of soda, but having the shape of four-sided prisms, acuminated with four planes; or of six-sided prisms, acuminated by six planes. It is deliquescent, and affords a thick syrupy liquor, which gives a green colour to the skin. It dissolves readily in water and alcohol, producing cold. When dilute acids are added to the solution, a brisk effervescence is excited, but no sulphur is deposited. Vauquelin found that its solution in water may be evaporated to dryness, without decomposing the hydro-sulphuret; for on heating the residuum, mixed with sulphur, in a retort, sulphureted hydrogen gas was disengaged abundantly

H. DRO-SULPHURET OF SODA is a compound, which derives some importance from its being produced along with carbonate of soda, in several processes for decomposing the sulphate of soda.\* It is transparent at first, colourless, and crystallized in four-sided prisms, acuminated by four planes. It has an acrid and alkaline taste, which soon becomes very bitter. Its solution is colourless, but tinges the skin or paper green. It effervesces briskly with acids, and no sulphur is deposited unless the nitric or oxymuriatic acids are added, which attract the hydrogen, and throw down sulphur.

Vauquelin has proposed to distinguish these two sulphurets, which so closely resemble each other, by the following test. The hydro-sulphuret of potash, when added to a solution of sulphate of alumine, occasions a crystallization of alum; but that of soda

has no such action.

Hydro-sulphuret of ammonia may be formed by the direct mixture of sulphureted hydrogen and ammoniacal gases in a dry vessel, cooled externally by ice. It is deposited in needle-shaped crystals. But, for all practical uses, it is better prepared, by putting a solution of pure ammonia into the middle vessel of a Nooth's machine, and passing through it streams of sulphureted hydrogen gas, till the liquid acquires a yellowish colour. In this state it constitutes the hepatized ammonia, so strongly recommended by Dr. Rollo as a remedy for diabetes.

HYDRO-SULPHURETS OF BARYTES AND STRONTIFES are crystallized salts, having a white silky lustre, and readily soluble in water.

HYDRO-SULPHURET OF LIME, formed by transmitting sulphureted hydrogen through water, in which lime is kept mechanically suspended, composes a crystallizable salt, soluble in water; and having the general properties of hydro-sulphurets.

# ART. 4.—Super-Sulphureted Hydrogen, and Hydrogureted Sulphurets.

I. Super-sulphureted hydrogen is obtained, when hydro-sulphuret of potash is poured, by little and little, into muriatic acid. A very small portion only of gas escapes; and while the greater part of the sulphur separates, one portion of it combines with the sulphureted hydrogen; assumes the appearance of an oil; and is deposited at the bottom of the vessel. Or, dissolve sulphur in a boiling solution of pure potash; and, into a phial containing about one-third its capacity of muriatic acid, of the specific gravity 1.07, pour about an equal bulk of the liquid hepar. Cork the phial, and shake it; the hydrogureted sulphur gradually settles to the bottom in the form of a brown, viscid, semifluid mass. Its properties are the following:

<sup>\*</sup> Annales de Chimie, lxiv. 59. † Ibid. lxii. 181. † This account differs in some respects from that of Vauquelin, Ann. de Chim. et Phys. vi. 37.

1. If gently heated, sulphureted hydrogen gas exhales from it; the super-sulphuret loses its fluidity; and a residue is left, consisting merely of sulphur.

2. It combines with alkalies and earths; and forms with them a

class of substances called hydrogureted sulphurets.

3. It is constituted, according to Mr. Dalton, of two atoms of sulphur, weighing 30, with one atom of hydrogen, and consists, therefore, per cent. of

Sulphur - - 96.75 Hydrogen - - 3.25

There are, therefore, three distinct combinations of sulphur and its compounds with alkalies and earths. The first consist, simply, of sulphur, united with an alkaline or earthy base, and are properly called sulphurets. The second are composed of sulphureted hydrogen, united with a base, and are called hydro-sulphurets. The third contain super-sulphureted hydrogen, attached to a base,

and constitute hydrogureted sulphurets.

The pure sulphurets can exist, as such, only in a dry state; for the moment they begin to dissolve in water, a decomposition of that fluid commences; sulphureted hydrogen is formed; and of this a part is disengaged, while another part, uniting with an additional proportion of sulphur, composes super-sulphureted hydro-This last, uniting with the base, forms an hydrogureted sulphuret. At the same time, it has been stated by Berthollet,\* sulphuric acid is composed, by the action of the sulphur on the oxygen of the water. This however, Gay Lussac has shown, takes place only when the sulphuret has been formed at an unnecessary degree of heat, and that when carefully prepared at a heat below redness, the solution of an alkaline sulphuret in water contains sulphurous and hypo-sulphurous acids, but no sulphuric acid.† The sulphurets, also, being partly changed, by solution, into hydrogureted sulphurets, the effusion of an acid throws down a quantity of sulphur. A distinguishing character, also, of solutions of this kind, is that sulphur is precipitated by passing through them sulphureted hydrogen gas.

According to Proust, if red oxide of mercury be added to solutions of the kind which have just been described, the sulphureted hydrogen is removed, and what remains is a pure liquid sulphuret, from which acids precipitate sulphur only, without any

effervescence.

II. The hydrogureted sulphurets are also formed by boiling along with a sufficient quantity of water, the alkaline, or earthy base, with flowers of sulphur. Thus a solution of pure potash, pure soda, or of barytes or strontites, may be changed into an hydrogureted sulphuret. To prepare this compound, with base of lime, the powdered earth, mixed with sulphur, may be boiled with

<sup>\*</sup> Ann. de Chim. xxv. 239, 269. † 6 Ann. de Chim. et Phys. 322.

a proper quantity of water, and the solution filtered or cleared by subsidence. One hundred grains of lime, or 134 of hydrate, dissolve about 215 of sulphur, and afford a liquid of 1.146 specific

gravity.

The hydrogureted sulphuret of ammonia (which base cannot, in strictness, owing to its liquid form, compose a true sulphuret) may be prepared as follows: Mix together, in a mortar, three parts of hydrate of lime, one part of muriate of ammonia, and one of flowers of sulphur. Introduce the mixture into a retort, and apply a receiver. Begin the distillation with a gentle heat. The first liquor, that comes over (long known under the name of Boyle's Fuming Liquor), has a light yellow tinge, and emits fumes; the second has a deeper colour, and is not fuming. When the latter begins to appear, the fire may be raised.

Another method of forming, by a very simple process, the hydrogureted sulphurets, consists in digesting, in a gentle heat, a hydro-sulphuret with powdered sulphur, an additional portion of which is thus dissolved, while part of the sulphureted hydrogen

escapes.

Hydrogureted sulphurets have the following properties:

7 1. They have a deep greenish yellow colour, and acrid and intensely bitter taste; and an excessively offensive smell.

2. They deposit sulphur when kept in close vessels; become much more transparent and lighter coloured; and less offensive to the smell.

3. They rapidly absorb oxygen from the atmosphere, and from

oxygen gas. Hence their employment in eudiometry.\*

4. On the addition of dilute sulphuric, or muriatic, or of certain other acids, they are decomposed. Sulphureted hydrogen gas is evolved, and sulphur is precipitated.

5. When boiled in contact with filings of silver or of copper, and of those metals only, Vauquelin found that they lose their

excess of sulphur, and become simple hydro-sulphurets.

Hydrogureted sulphurets of potash and of soda differ very little from each other. They may be formed by boiling solutions of pure potash or soda with flowers of sulphur. When very concentrated, they have a deep reddish brown colour, a nauseous taste, a disagreeable odour, and a soapy feel, tinging the cuticle black. When exposed to the air, a thin pellicle of sulphur forms upon their solutions, which, by sufficiently long exposure, are changed into sulphates. When and acid is suddenly added, sulphur is thrown down, which becomes, when washed with sufficient water and dried, almost white, and constitutes what has been called precipitated sulphur, milk of sulphur, or magistery of sulphur.

HYDROGURETED SULPHURET OF AMMONIA may be formed by the process already described, or by digesting hydro-sulphuret of am-

monia with sulphur, a portion of which is dissolved.

HYDROGURETED SULPHURET OF BARYTES is obtained by boiling crystals of pure barytes with one fourth their weight of sulphur and sufficient water. Two compounds are formed, viz. an hydrogureted sulphuret, which has a red colour and remains in so-

<sup>\*</sup> See chap. v. sect. 4.

lution; and colourless crystals, which are supposed to be a hydrosulphuret of barytes. Strontites forms similar compounds.

Hydrogureted sulphuret of lime is formed by boiling hydrate of lime with a third its weight of sulphur and ten times its weight of water. The compound has a deep orange colour, and is of importance from its application to eudiometrical purposes. From the experiments of Vauquelin, it appears probable, that the proportion of its ingredients varies, and is attended with corresponding differences of solubility and other properties.\*

# Sulphuret of Carbon, or Alcohol of Sulphur.

There has been much controversy respecting the nature of this compound; and several contradictory statements have been given of its composition. It was discovered by Lampadius in 1796, and was considered by him as consisting of sulphur and hydrogen. Clement and Desormes were led, by their researches, to deny the presence of the latter element; and to conclude that it is a compound of sulphur and charcoal. This inference was afterwards . controverted by Vauquelin and by Berthollet, jun.; and the experiments of Cluzel also were supposed by their author to be favourable to the opinion, that it contains hydrogen.t In a report, however, on the memoir of Cluzel, MM. Berthollet, sen. Thenard, and Vauquelin describe experiments made by the last-mentioned chemist, which lead them to believe that the alcohol of sulphur is a true binary compound of sulphur and charcoal only;t and this inference has been proved to be correct, by the recent and able investigations of Drs. Berzelius and Marcet §

To prepare this substance, a coated earthen tube, of about one inch and a half in diameter, partly filled with small pieces of charcoal, may be disposed in a furnace as represented fig. 40, cc, one end being placed higher than the other. To this end may be adapted a glass tube, open at both ends, containing small bits of sulphur; and, to the other end, by means of an adopter, is to be fixed a curved tube, passed into water contained in a two-necked bottle. The part of the tube, containing the charcoal, may then be made red-hot; and, when this happens, the bits of sulphur are to be pushed forwards, one by one, by means of a wire, carefully excluding air. As soon as the sulphur comes into contact with the charcoal, bubbles of gas will be produced in great abundance, and a vapour will appear, which will condense, under the water in the bottle, into a liquid, of which, in the course of a day, about half a pint may be procured. This liquid may be purified by redistilling it at a very gentle heat, not exceeding 100° or 110° Fahrenheit: and some dry muriate of lime may be put into the retort, in order to obtain the fluid perfectly free from water. The liquid which comes over is quite pure, and some sulphur remains in the

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<sup>\*</sup> Ann. de Chim. et Phys. vi. 39.

Ann. de Chim. lxxxiii. 252.

<sup>†</sup> Ann. de Chim. lxxxiv. 73. § Phil. Trans. 1813.

The alcohol of sulphur has the following properties:

1. It is eminently transparent, and perfectly colourless. times, immediately after distillation, the oily liquid appears a little opaque and milky; but the next day it is found to have become completely limpid. It has an acrid, pungent, and somewhat aromatic taste; its smell is nauseous and fetid, though differing from

that of sulphureted hydrogen.

2. Its specific gravity is 1.272; its refractive power, as ascertained by Dr. Wollaston, is 1.645. Its expansive force (at 30 inches barometer, and 53½° Fahrenheit) is equal to the pressure of 7.36 inches of mercury; so that air, to which it is admitted, will dilate about one fourth of its volume. It boils briskly under the common atmospheric pressure, at a temperature of 105° or 110° Fahren-It does not congeal, at a temperature as low as 60° below of Fahrenheit.

3. It is highly inflammable, and takes fire at a temperature scarcely exceeding that at which mercury boils. Its flame is bluish, and it emits copious fumes of sulphurous acid. If a long glass tube, open at both ends, be held over the flame, care being taken to keep the tube quite cool, no moisture whatever is deposited on its inner surface, a sufficient proof of the absence of hydrogen.

The oily liquid readily dissolves in alcohol and ether, though not in all proportions, and these solutions are decomposed by the addition of water. It readily incorporates with fixed and volatile oils,

and rapidly dissolves camphor. It is not soluble in water.

5. In its liquid state, it suffers no change on being heated with potassium; but potassium, when heated in its vapour, becomes ignited, and emits a reddish flame. The residue, when washed with water, affords sulphuret of potash and charcoal.

6. It does not tarnish mercury or its amalgams, nor silver, unless it contain more sulphur than is essential to its constitution.

7. The alkalies dissolve it entirely, but very slowly. Of the acids, none exert any sensible action on it, but the nitro-muriatic and liquid oxymuriatic acids, which occasion its decomposition.

8. When transmitted over ignited copper or iron turnings, alcohol of sulphur is decomposed, the metal combining both with charcoal and sulphur; and a rose coloured fluid is obtained, differing in its sensible qualities from the original liquid, and apparently consisting of the same elements in different proportions.

The proportions of the elements of sulphuret of carbon are deduced by Berthollet, Thenard, and Vauquelin, to be from 14 to 15 parts of charcoal, and from 85 to 86 of sulphur, in 100. statement of its composition nearly agrees with that inferred by

Drs. Berzelius and Marcet; viz.

The above-mentioned numbers establish the proportion of the elements of this compound to be two atoms of sulphur to one of carbon.

The sulphuret of carbon was found by Berzelius to be capable of uniting with alkaline and earthy bases, and of forming compounds which may be called *Carbo-Sulphurets*. But their properties, and the proportion of their elements, require further investigation.

In a subsequent memoir in the same volume of the Philosophical Transactions, Dr. Marcet describes the extraordinary power of alcohol of sulphur, in producing cold. The bulb of a thermometer being covered with fine lint, and moistened with a few drops of the liquor, the mercury sinks rapidly from 60° to 0, and under the exhausted receiver of an air pump, from + 70°, to 70° or even 80° below, so that by this process mercury may readily be frozen.

## CHAPTER XIII.

COMBINATION OF NITROGEN WITH OXYGEN, CONSTITUTING NITRIC ACID,—NITROUS GAS,—NITROUS OXIDE,—AND COMPOUNDS OF NITRIC ACID WITH ALKALIES.

When nitrogen and oxygen gases are mingled together, in whatsoever proportions they are employed, no combination ensues. The result is a simple mixture of the two gases, which do not, like inelastic fluids, separate on standing, but remain diffused through each other for an indefinite length of time. This is the case with the air of our atmosphere; and it is fortunate that such a provision of nature exists, since the atmosphere contains the elements of several combinations which, if actually formed, would be fatal to animal and vegetable life. When, however, either one or both of these elements is in a condensed state, or deprived of part of that caloric which keeps the particles of all gases at a distance from each other, they unite and form compounds, distinguished by very striking properties. According to the proportions in which the oxygen and nitrogen exist in these compounds, their qualities undergo a remarkable variation, so that from two elementary bodies, variously united, we have several compounds, totally unlike each other in external qualities, as well as in their chemical relations.

Before describing the compounds of oxygen and nitrogen individually, it will contribute to perspicuity to take a general survey of the whole. Some of them exist essentially in an aëriform state, and are capable of uniting with water and other liquids in only small proportions. Others, again, combine with water to such an extent, that the liquid form is the only one under which they occur to our observation. When entirely deprived of water, they are all essentially gaseous bodies.

In a series of the compounds of nitrogen, founded on their proportion of oxygen, they occupy (excluding atmospherical air from the number) the following order, the last containing the largest proportion of oxygen-nitrous oxide-nitric oxide or nitrous gasper-nitrous acid—nitrous acid or nitrous vapour—and nitric acid. The two first are sparingly soluble in water; but the three last unite with it largely, and form liquid compounds of decidedly acid taste and quality.

The following Table exhibits the composition of three of these bodies, the calculation being founded on the experiments of Sir H. Davy, published in the year 1800 in his "Researches." Oxygen gas is assumed to weigh 33.8 grains, and nitrogen, 29.5 for

100 cubical inches.

		Proport Elements b				Proportion by Measure.			
Nitrous oxide.		Nitrogen.	Oxygen. 36.70			Nitr. gas.	Ox. gas. 50.63		
gas .		44.05	55.95	•		100.	110.		
Nitrous acid*.		29.50	70.50	•	•	100.	208.60		

From a comparison of the third and fourth columns of the foregoing Table, it is obvious, that in nitrous oxide, the nitrogen is, in volume, very nearly double the oxygen; that in nitrous gas, the two elements exist in almost equal volumes; and that in nitrous acid, the oxygen is a little more than twice the volume of the nitrogen. These coincidences, and others of the same kind, are the foun. dation of the theory advanced by Gay Lussac; viz. that compounds, whose elements are gaseous, are constituted either of equal volumes of those elements; or, that if one of the elements exceeds the other, the excess is by some simple multiple of its volume. That the proportions of nitrogen and oxygen by measure do not, in the foregoing instances, exactly conform to this law, is ascribed by Gay Lussac to unavoidable inaccuracies, attendant on all delicate processes for determining the constitution of gaseous bodies. In one instance, this was proved experimentally; for M. Berard, by the combustion of potassium in 100 measures of nitrous gas, obtained exactly 50 measures of nitrogen. Hence the table, corrected to coincide with the views of Gay Lussac, and enlarged so as to comprehend all the known compounds of nitrogen, will stand as follows:

					Measu	res of			100 grains contain				
Nitrous oxide	COL	sis	ts	of	Nitrogen.	Ozygen. 50		•		Nitrogen. 63.58	Oxygen. 36.42		
gas .						100		•		46.60	53.40		
Per-nitrous aci	d.				100	150	ċ			42.02	57.98		
Nitrous acid.			•,		100	200	•		•	30.40	69.60		
Nitric acid .	•	•	•		100	250	•	•	•	25.97	74.03		

<sup>\*</sup> These were at first stated to be the proportions of the elements of nitric acid; but they apply more correctly to nitrous acid.

Supposing the foregoing proportions by volume to be correct, the proportions by weight will be as follows:

														In weight of			
· <b>U</b>									Nitrogen.		Oxygen.						
Nitrous oxide consists o	f		•.				•	•	100	+	57						
gas						•			100	+	114						
Per-nitrous acid																	
Nitrous acid									100	$\dot{+}$	228						
Nitric acid								•	100	+	285						

In all these compounds, the elements are in a state of condensation, except in nitrous gas, in which the nitrogen and oxygen, according to Gay Lussac, are precisely in the same state of density, as in nitrogen and oxygen gases. In the other compounds, the contraction, he apprehends, is exactly equivalent to the bulk of the oxygen gas. For example, in 100 measures of nitrous oxide, consisting of 100 measures of nitrogen gas and 50 measures of oxygen gas, the condensation is 50 measures. On the same principle 100 measures of nitrogen gas and 200 of oxygen gas constitute 100 of nitrous acid gas; and 100 measures of nitrogen and 250 of oxygen compose 100 of gaseous nitric acid.

Mr. Dalton, in his "New System of Chemical Philosophy," has given a Table of the Compounds of nitrogen and oxygen, which differs essentially from that of Gay Lussac. This table, however, it is unnecessary to copy, because it has been since materially altered by the author, who has presented it under the following corrected form.\*

	Volumes of	Atoms of	Symbolt
	Nitrogen. Oxygen.	Nitrogen. Oxygen.	
Nitrous oxide .	. 100 + 62	2 + 1	$\infty$
gas	· 100 <del>+</del> 124	1 + 1	$\infty$
Per-nitrous acid	100 + 186	2 + 3	<b></b>
Nitrous acid .	100 + 248	1 + 2	$\infty$
Nitric acid	100 + 310	2 + 5	တ္ထာ

It will be obvious, from a comparison of this table with the foregoing one, that it assigns to all the compounds of nitrogen, 24 percent. or very nearly one fourth, more oxygen, than is stated by Gay Lussac to enter into their composition. It is admitted, on all hands, that setting out from nitrous oxide, the other compounds of

<sup>\*</sup> Thomson's Annals, ix. 193. † O representing oxygen, and () nitrogen.

correct one, and that

nitrogen contain proportions of oxygen, which are simple multiples, both in weight and in volume, of that existing in nitrous The question, which is still disputed by the opponents of the theory of volumes, is whether it be true that one volume of nitrogen unites with either exactly half a volume of oxygen, or with exactly an equal volume, or a double volume, and so on. Analogy is certainly in favour of this opinion; for the instances are numerous, in which gaseous bodies observe the law respecting volumes, deduced by Gay Lussac; and we have not, at present, any well ascertained exception to it. The argument, which, perhaps, weighs most in its favour, when applied to the combinations of nitrogen and oxygen, is that, assuming nitrous oxide to consist of one volume of nitrogen and half a volume of oxygen, and multiplying the oxygen of nitrous oxide by 5, we are led to proportions constituting nitric acid, which almost exactly agree with those deduced by Dr. Wollaston from the experiments of Richter and Phillips.

If it should, hereafter, be unquestionably established that the elements of the compounds of nitrogen and oxygen are truly expressed by the table of Gay Lussac, it will then follow that the number representing the atom of nitrogen (oxygen being taken at 7.5) must be 13, or (oxygen being 10) 17.5. In this determination, it is taken for granted that the two elements exist atom to atom in nitrous oxide, and that this, and not nitrous gas, is the true binary compound. But if, with Mr. Dalton, we suppose nitrous oxide to be constituted of two atoms of nitrogen to one of oxygen, we must then express the weight of the atom of nitrogen, either by  $13 \div 2 = 6.5$ , or, taking oxygen at 10, by  $17.5 \div 2 = 8.75$ . It appears to me, however, most probable, that the former view is the

Nitrous oxi	de	con	sis	ts	of	1	a	tom	of	ni	tro	gen	+	ı	of	ox	yge	n.	:
Nitrous gas			•			1		•			•	•	+	2	٠.	•	`.		
Per-nitrous	acio	d '.				1	•			÷	•		+	3	٠.				
Nitrous acid	Ι.	•				1				• ,	•		+	4					
Nitric acid																			

It is obvious that as the five compounds of nitrogen and oxygen, which have been already described, contain the same elements, and differ only in their proportion, they may be converted into each other, by adding or subtracting a due proportion of oxygen. Thus nitric acid, by contact with some of the oxidizable metals, is converted into nitrous gas; and nitrous gas, by abstracting a farther quantity of oxygen, is changed into nitrous oxide. Again, by adding oxygen to nitrous gas, it may be reconverted into pernitrous, nitrous, or nitric acid, according to the proportion of oxygen which is added, and the circumstances under which the combination is effected.

### SECTION I.

#### Nitric Acid.

I. The direct combination of nitrogen and oxygen, affording a decisive synthetic proof of the nature of this acid, may be effected by passing electric sparks through a mixture of nitrogen and oxygen gases. The experiment is an extremely laborious one, and requires, for its performance, a powerful electrical machine; but those who are disposed to repeat it, may proceed as follows:

Let the tube, fig. 84 c, be filled with, and inverted in, mercury. Pass into it a portion of atmospherical air, or an artificial mixture of nitrogen and oxygen gases, in the proportion of one of the former to two of the latter.—Let an iron wire, lengthened out with one of platinum, be introduced within the tube, so that the latter metal only may be in contact with the mixed gases; and let the end of this wire be distant about one fourth of an inch from the extremity of the upper conducting one. When the apparatus is thus disposed, pass a series of electric sparks or shocks through the gases for several hours. The mixture will be diminished in bulk; will redden litmus-paper when enclosed in it; and will exhibit distinctly the smell of nitrous acid. If the experiment be repeated, with the addition of a few drops of solution of potash, in contact with the gases, we shall obtain a combination of nitric acid with potash.

This interesting experiment on the generation of nitric acid we owe to Mr. Cavendish, who discovered the fact in the year 1785\*. The proportions, which he found to be necessary for mutual saturation, were five parts of oxygen gas and three of common air, or seven parts of oxygen gas to three of nitrogen gas. The acid, thus obtained, being constituted of 100 measures of nitrogen + 233 oxygen, appears therefore to have been intermediate between nitrous and nitric acid, or more probably consisted of both those acids in a state of mixture. No evolution either of light or heat attends this combination, which is very slowly and gradually

effected.

Another synthetic proof of the production of nitric acid will be stated under the article nitrous gas. It is furnished by the generation of nitrous gas, and ultimately of nitric acid, when ammonia is brought into contact with the black oxide of manganese.

For all purposes of utility or experiment, however, nitric acid is prepared in a different manner, viz. by the decomposition of nitrate of potash, in a way which will be described in the section on that

II. The analysis of the nitric acid may be obtained by driving

<sup>\*</sup> Philosophical Transactions, lxxv.

its vapour through a red hot porcelain tube (fig. 40, cc,) and receiving the generated gases, which prove to be a mixture of nitrous acid, oxygen, and nitrogen gases.

III. The liquid nitric acid has the following properties:

(a) It is heavier than water, in the proportion of 1.5 or upwards to 1. Proust obtained it as high as 1.62; and the specific gravity of real nitric acid, which cannot, however, be obtained separately, may be calculated at 1.75. In its heaviest form, it still contains a portion of water, which is essential to its existence in a liquid state, and without which its elements would separate from each other. In acid of the sp. gr. 1.50, the water amounts, calculating from the data furnished by Dr. Wollaston, to 25.11 grains in 100 grains of acid; or according to Mr. R. Phillips to 25.09.

Pure nitric acid may be considered as a gaseous body, of the specific gravity, compared with common air, of 2440: one hundred cubic inches, at 55° Fahrenheit and under 30 inches pressure, weigh, according to Sir H. Davy, 76 grains; or corrected to the temperature of 60° Fahrenheit, they weigh 75.21 grains. liquid acid (termed by Davy hydro-nitric acid) consists of this gas condensed by water, of which it contains various proportions. We have not, however, at present, documents sufficient for the construction of an accurate Table of the quantities of real nitric acid in acids of different densities. According to Sir H. Davy, the strongest acid (sp. gr. 1.55) contains 14.4 parts of water in 100; and acid of sp. gr. 1.42 contains 25.2 of water in 100.\* The Table published by Mr. Dalton† that philosopher has since found reason to believe to be inaccurate; but the following results, which he has been so good as to communicate to me, he thinks are entitled to greater confidence.

Table of the quantity of real Acid in Nitric Acid of different densities.

Parts of Acid.		Parts of Water.	Acid per ct. by weight.	Acid per ct. by measure.	Specific Gravity.
45	+	8	84.9	137.5?	1.62?
45	÷	16	73.8	114.4?	1.55?
45	÷	24	65.2	96.4	1.48+
45	÷	32	58.4	84.	1.44
45	+	<b>4</b> 0 .	53.	74.7	1.41
45	÷	48	48.4	67.2	1.39
45	$\dot{+}$	56	44.5	60.5	1.36
45	$\dot{+}$	64	41.3	55.3	1.34
45	÷	180	20.	22.8	1.142

The Table of Mr. Dalton, Dr. Ure believes, however, to be deficient in accuracy, and he has constructed two others (for which

<sup>\*</sup> Elements, p. 265.

<sup>†</sup> New System, p. 355.

see the Appendix,) the first from experiments on the mixture of nitric acid of specific gravity 1.500 with water, in the proportions of 95 + 5, 90 + 10, 80, + 20, &c.; and the second from the calculation of the intermediate terms by a law of progression, which may be thus stated: The specific gravity of dilute acid, containing 10 parts in the hundred of acid of density 1.500, is by experiment 1.054. Taking this number as the root, its successive powers will give us the successive densities, at the terms of 20, 30, 40 per cent. &c. Thus  $1054^2 = 1.111$  is the specific gravity corresponding to 20 strong acid + 80 water;  $1054^3 = 1.234$  the density of 30 strong acid + 70 water; and hence any one term being given the whole series may be found.

(b) Pure gaseous nitric acid, according to the experiments of Sir H. Davy, published in the year 1800, is composed in 100 grains, of 29½ azote, and 70½ oxygen. This approximation differs but little from the proportions deducible from the synthetic experiments of Cavendish, viz. 27.8 nitrogen to 72.2 oxygen. The later results of Sir H. Davy have led him, however; to believe, that 4 in volume of nitrous gas and 2 of oxygen gas, when condensed in water, absorb 1 in volume of oxygen to become nitric acid. Now, estimating the oxygen gas, existing in nitrous gas, at one half its volume, and taking the specific gravities of oxygen and nitrogen gases at the numbers already given, 100 parts by weight of nitric acid will consist of

Oxygen Nitrogen						
7						
			100			986

In investigating what number should be used as the equivalent of nitric acid, Dr. Wollaston was led to inquire into the composition of that acid; and, from his own experiments, and those of Richter and Phillips, he infers the oxygen, which nitric acid contains, to be by weight to the nitrogen, as 50 to 17.54. Hence nitric acid, as it exists in nitre, will be composed by weight of

Oxygen												
Nitrogen	•	•	•-	25.97	•	•	. •	35	;	•	•	100
				100-				135				38 <b>5</b>

By an easy caculation, it will be found that the nitrogen, in 100 grains of nitric acid thus constituted, is equal in volume to 88 cubic inches, and the oxygen to 219. But as 88 to 219, so is 100 to 249; and on this view of the nitric acid, it is composed of 1 volume of nitrogen and 2½ of oxygen, which agrees with the result of Sir H. Davy, and with the latest determination of Gay

Lussac.\* These proportions appear on first view to be favourable to the opinion, that nitric acid consists of two atoms of oxygen to one of nitrogen; for as 75 to 25, so is 15 (twice 7.5) to 5, the number already deduced from the analysis of ammonia, as representing the weight of the atom of nitrogen. It must be acknowledged, that there is some uncertainty respecting the weight of the atom of that element. Dr. Wollaston deduces its equivalent (oxygen being 10) to be 17.54; and hence the atom of nitrogen will bear to that of oxygen the proportion of 13.15 to 7.5; and nitric acid, according to this view, will consist of 5 atoms of oxygen = 37.5, and 1 atom of nitrogen = 13.15; and its atom will weigh 50.20. Farther investigation must determine, which of these views is most conformable to truth.

(c) Hydro-nitric acid is perfectly limpid and colourless, and emits white fumes, when exposed to the air.

(d) It gives a yellow stain to the skin.

(e) It boils at 248° Fahrenheit, and may be distilled over, without any essential change. This, however, is true only of acid of the specific gravity 1.42; for an acid, weaker than this, is strengthened by being boiled; while an acid, stronger than 1.42, becomes weaker by boiling. All the varieties of nitric acid, therefore, are

brought, by sufficient boiling, to the specific gravity 1.42.

(f) Hydro-nitric acid may be frozen by the application of a sufficiently low temperature. Like sulphuric acid, there is a certain point of density, at which it most readily congeals. Mr. Cavendish has described this, not by its specific gravity, but by the quantity of marble which it is capable of dissolving. When it takes up four hundred and eighteen 1000ths of its weight, in which case its specific gravity is 1.3, the acid freezes at 2° below 0 Fahrenheit. When considerably stronger and capable of dissolving five hundred and sixty-one 1000ths, it required cooling to — 41.6; and when so much diluted as to take up only two hundred and seventy-six 1000ths, it did not congeal till cooled to — 40.3.†

(g) Strong hydro-nitric acid absorbs moisture from the atmosphere; in consequence of which it increases in weight, and dimi-

nishes in specific gravity.

(h) When two parts of the acid are suddenly diluted with one of water, an elevation of temperature is produced to about 112° Fahrenheit; and the admixture of 58 parts by weight of acid of specific gravity 1.50 with 42 parts of water, both at 60° Fahrenheit, gives a temperature of 140°.‡ When more water is added to this diluted acid, its temperature is reduced. Snow or ice added to the cold dilute acid is instantly liquefied, and an intense degree of cold is produced.

(i) It becomes coloured by exposure to the sun's light, passing first to a straw colour, and then to a deep orange. This effect is

<sup>\*</sup>Ann. de Chim. et Phys. i. 404. † Phil. Trans. 1788. † Dr. Ure, Journ. of Science, iv. 298.

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produced by the union of the light of the sun with oxygen, in consequence of which the proportion of the acidifying principle to the nitrogen is diminished.

By exposing it to the sun's rays in a gas bottle, the bent tube of which terminates under water, oxygen gas may be procured.

(k) This acid retains its oxygen with but little force.—Hence it is decomposed by all combustible bodies, which are oxygenized by it, with more or less rapidity in proportion to their affinity for

oxygen.

1. When brought into contact with hydrogen gas at a high temperature, by transmitting them through an ignited porcelain tube, a violent detonation ensues. This experiment, therefore, requires great caution. 2. Poured on perfectly dry and powdered charcoal, it excites the combustion of the charcoal, which becomes red-hot, and emits an immense quantity of fumes. 3. It also inflames essential oils (as those of turpentine and cloves,) when suddenly poured on them. In these experiments, the acid should be poured out of a bottle, tied to the end of a long stick; otherwise the operator's face and eyes may be severely injured. 4. Nitric acid is decomposed, by boiling it in contact with sulphur, which attracts the oxygen, and forms sulphuric acid.

(1) The hydro-nitric acid is also decomposed by metals; as iron, tin, zinc, copper, &c.; and with different phenomena, according to the affinity of each metal for oxygen. This may be seen, by pouring some strong nitric acid on iron filings, or powdered tin. The acid must be of greater density than 1.48, otherwise it will not produce the effect. Violent heat, attended with red fumes, will be

produced, and the metals will be oxydized.

(m) If the action of metals on nitric acid be more moderately conducted, a new product is obtained in a gaseous state. Dilute some nitric acid of commerce with 6 or 8 parts of water, and dissolve, in this, some turnings of copper, or a portion of quicksilver, applying a gentle heat.—This must be done in a gas bottle, and the product, received over water, is nitrous gas, or nitric oxide. Mr. Dalton recommends acid, of density 1.2 or 1.3 to be poured on filings of copper, without any other heat than that which the action of the acid and metal on each other occasions.

#### SECTION II.

# Nitrous Gas, or Nitric Oxide.

THE properties of this gas, procured in the manner described at the close of the last section, are the following:

(a) It is permanent over water; but it is absorbed in the proportion of about 1 volume to 18 or 20 water, when agitated with water which has been recently boiled, and has become cold. This

solution, according to La Grange, is converted, by long keeping, into nitrate of ammonia, in consequence of the decomposition of the water.

Nitrous gas is rather heavier than common air. One hundred cubic inches at 55°, barometer 30°, were stated by Sir H. Davy in 1800, to weigh 34.26, or at 60° Fahrenheit 33.80 grains. He now, however, gives the weight of 100 cubic inches at 32 grains, and hence its specific gravity is 1.050. Berard's determination is considerably lower; viz. 1.0388 by experiment, or 1.0364 corrected by calculation.

(b) When well washed with water, it is not acid. It will be found not to redden the colour of litmus. This may be shown by introducing a piece of paper, tinged with that substance, into a jar of nitrous gas, standing inverted over water. To accomplish this, the paper should be fastened to the end of a glass rod or a piece of stick. The colour will remain unchanged.

(c) It extinguishes flame, and is fatal to animals. Homberg's pyrophorus, however, is inflamed by it; and charcoal and phosphorus, introduced into it when in a state of actual combustion,

continue to burn vehemently.

(d) Mingled with hydrogen gas, it imparts a green colour to its flame. It does not, however, explode with hydrogen in any proportion, nor with any of the varieties of carbureted hydrogen. But, when mixed with ammonia, an electric spark produces a detonation, as I have shown in the Philosophical Transactions for 1809. The proportions required for mutual saturation are about

120 measures of nitrous gas to 100 of ammonia.

(e) When mixed with oxygen gas, red fumes arise; heat is evolved; a diminution takes place; and if the two gases be in proper proportion, and perfectly pure, they disappear entirely. Ten measures of oxygen, Mr. Dalton asserts, may be made to condense any quantity of nitrous gas, between 13 and 36 measures, accordingly as the mixture is conducted; and Gay Lussac finds that 100 measures of oxygen gas condense over water from 134 to 365 nitrous, but in a dry glass vessel only 204, which, allowing for inaccuries, may be stated at 200. In the latter case the total 300 measures become 200 of nitrous acid vapour.

(f) The same appearances ensue, less remarkably, with atmospheric air; and the diminution is proportionate to the quantity of oxygen gas which it contains. On this property, of its condensing oxygen, but no other gas, is founded the application of nitrous gas to the purpose of eudiometry, or of ascertaining the purity of air. The sources of error, in its employment in this mode, have hitherto been considered such as to forbid our relying implicitly on the results which it may afford. Learning, however, from Mr. Dalton, that he constantly employs nitrous gas in determining the purity of air, and with perfect satisfaction as

to the accuracy of his results, I have obtained from him the following communication. It may be necessary to premise, that for applying nitrous gas to this purpose, two tubes will be found convenient, shaped like fig. 24; each from three to four tenths of an inch in diameter; eight or nine inches long, exclusive of the funnel-shaped part; and accurately graduated into minute aliquot parts. What these parts are, is of no consequence. Hundredth parts of a cubical inch give rather too large divisions of the scale; but if each of these be divided into two, the scale will be sufficiently small. If the tube employed be not long enough to comprise 100 of these parts, the experiment may be made on 50 parts only of atmospherical air; and the results, multiplied by 2, will give the proportion in 100 parts.

"To use nitrous gas accurately in eudiometry, it is only requi"site to take both gases in a dilute state, namely, containing four
"or five times their bulk of azotic gas (which atmospheric air na"turally does,) or of any other gas not acted upon by nitrous or
"oxygen gases. In this case, if an excess of one gas be used, the
"other is, in a few minutes, entirely taken up, and in a constant
"proportion; whatsoever may be the form of the vessel, or the
"manner of mixing the gases. The proportion is 1 of oxygen to
"1.7 of nitrous, so that 10-27ths of the diminution over water are
"oxygen, and 17-27ths nitrous gas. It is proper, as soon as the
"greater part of the diminution has ensued, to transfer the mix"ture through water into a graduated vessel, without using any
"agitation.

"If pure nitrous gas be admitted to pure oxygen gas in a nar"row eudiometer tube, so that the oxygen gas is uppermost, the
"two unite very nearly in the same uniform proportion as above.
"if, on the other hand, the nitrous be the upper gas, a much less
"quantity of it disappears, viz. 1.24 nitrous to one oxygen. If un"diluted nitrous gas be admitted to pure oxygen gas in a wide
"vessel over water, the whole effect takes place immediately; and
"one measure of oxygen will condense 3.4 nitrous gas.

"To render this rule more intelligible, an example may be ne"cessary. Let 100 measures of common air be admitted to 100
"measures of a mixture of nitrous gas, with an equal volume of
"azotic or hydrogen gas. After standing a few minutes in the
"eudiometer, there will be found 144 measures. The loss 56 be"ing divided by the common divisor, 2.7, gives 21 nearly for the
"oxygen gas present in 100 measures of common air."

To these directions I may add, that when atmospherical air is the subject of experiment, it is scarcely necessary to dilute the nitrous gas, with any other gas, previously to its use. If a number of experiments be made, it will be proper, in all cases, to let the gases remain together a definite time (say 10 minutes) before noting the diminution; and it is needless to transfer them into another vessel. If the mixed gas, under examination, contain much more oxygen than is present in atmospherical air, then it is proper

to dilute the nitrous gas with an equal bulk of hydrogen gas; and, in this case, the narrower the tube in which the experiment is made, the more accurate will be the result.

Subsequent experience has convinced me that the method, proposed by Mr. Dalton, though sufficiently correct when applied to a mixture of the same, or nearly the same, standard as the atmosphere, cannot be relied on when the proportion of oxygen is either considerably greater or less. In the former case, the process gives too great a diminution, sometimes indeed to such an extent as to indicate more oxygen gas than the whole amount of what was submitted to experiment. When the air, on which we are operating, is of an inferior standard to the atmosphere, we do not learn its full proportion of oxygen. Notwithstanding these objections, however, the method has considerable value, since it may be applied to determine the proportion of oxygen in some mixed gases, to which other eudiometrical tests are not applicable; for example, to mix-

tures of hydro-carburet and oxygen gases.

The application of nitrous gas to eudiometrical purposes, it has lately been contended by Gay Lussac, is susceptible of perfect accuracy, provided certain precautions be observed which he has pointed out, and which were suggested by his theoretical views of the constitution of these gases. A narrow tube he finds to be unfit for an eudiometer, his object being to form nitrous acid gas, which is but slowly absorbed by water. Instead therefore of a tube, we must take a wide vessel, such as a small tumbler glass; and to 100 parts of atmospheric air, previously measured, we must add at once 100 measures of nitrous gas. A red fume will appear, which will soon be absorbed without agitation, and in half a minute, or a minute at most, the absorption will be complete. Pass the residuum into a graduated tube, and it will be found, almost invariably, that 84 measures have disappeared. Dividing this number by 4, we have 21 for the quantity of oxygen condensed.

By a series of experiments on mixtures of oxygen and nitrogen gases in various proportions, Gay Lussac found that this eudiometrical process may be depended upon, whether the oxygen exceed or fall short considerably of the proportion contained in atmosphe-

ric air.

(g) The generation of an acid, by the admixture of nitrous gas with common air or oxygen gas, may be shown by the following experiment. Paste a slip of litmus paper within a glass jar, near the bottom; and into the jar, filled with and inverted in water, admit as much nitrous gas, previously well washed, as will displace the water below the level of the paper. The colour of the litmus will remain unchanged; but, on adding atmospheric air or oxygen gas, it will be immediately reddened.

(h) The acid, thus produced, is either nitric or pernitrous, according to the circumstances of the experiment, the presence of water favouring the production of the latter, and its absence promoting that of nitric acid.\* The nature of the product may be shown, in a general way, as follows: Into a jar, filled with and inverted in mercury, pass a small quantity of a solution of pure potash; and, afterward, measures of oxygen and nitrous gases, separately, and in proper proportion. On removing the solution from the jar, exposing it for some time to the atmosphere, and afterward evaporating it, crystals of nitrate of potash will be formed, a salt which is ascertained to be formed of potash and nitric acid.

(i) Nitrous gas is absorbed by hydro-nitric acid, which, by this absorption, is considerably changed in its properties. Transmit the gas, as it issues from the materials that afford it, through colourless nitric acid. The acid will undergo successive changes of colour, till at last it will become orange-coloured and fuming. In this state it is called nitrous acid, because it contains a less pro-

portion of oxygen than the colourless nitric acid.

According to Dr. Priestley, 100 parts of nitric acid, of the specific gravity of 14 to 10, absorb, in two days, 90 parts by weight of nitrous gas.† When about seven parts of gas have been absorbed, the acid acquires an orange-colour; when 18 have been absorbed, it becomes green; and the whole quantity, which it is capable of condensing, changes it into a liquor, which emits an immense quantity of red fumes. The gas, thus absorbed, is mostly separated again on dilution with water.

(k) The nitrous gas, thus absorbed, is expelled again by a gentle heat. This may be shown by gently heating the acid coloured in Experiment i, till it again becomes limpid. In this experiment

light should be excluded.

(1) Nitrous gas is decomposed by exposure to bodies that attract oxygen. Thus, iron filings decompose it, and become oxydized, affording a proof of the presence of oxygen in this gas. During this process, water, ammonia, and nitrous oxide, in the proportion of one volume from two of nitrous gas, are generated. Sulphuret of potash, &c. have a similar effect. Sulphuret of barytes gives one half its volume of nitrogen. Mixed with sulphurous acid, nitrous gas is decomposed, and this acid is changed into the sulphuric, but not unless water is present. Nitrous gas does not with hydrogen gas afford a mixture that can be exploded by the electric spark; but with ammoniacal gas it may be fired in a Volta's eudio-

<sup>\*</sup> Dalton, in Thomson's Annals, x. 39.

<sup>†</sup> Priestley on Air, 2d. edition, i. 383. In the experiment alluded to, one fifth of an ounce-measure of nitric acid absorbed 130 ounce-measures of nitrous gas; or more than 60 per cent. by weight. There is reason, however, to suspect some inaccuracy in the experiment; for according to Sir H. Davy, 100 parts of nitric acid, after having absorbed all the nitrous gas which it is capable of condensing, hold only nine or between nine and ten parts in combination, and Mr. Dalton could not condense more than 20 times its bulk, or a little more than 2 per cent. by weight, of nitrous gas, into acid of the specific gravity 1.3.

<sup>†</sup> Nicholson's Journal, xvii. 43.

meter over mercury. The oxygen of the nitrous gas unites with the hydrogen of the ammonia, and the nitrogen of both gases is set at liberty.

Bodies that have a still more powerful affinity for oxygen decompose nitrous gas into its *ultimate* elements. Charcoal ignited in 100 measures, gives 50 measures of nitrogen gas, and 50 of carbonic acid. Arsenic, zinc, or potassium, when heated in it, evolve half its volume of nitrogen. Nitrous gas should consist, therefore, of 1 volume of oxygen + 1 volume of nitrogen, neither of which elements is in a state of condensation. This, however, would lead to a determination of the weight of the atom of nitrogen, very different from that already deduced from the composition of ammonia and of nitric acid. For if nitrous gas be constituted, as Mr. Dalton supposes, of an atom of each of its elements, and if these exist in it in equal volumes, the atom of oxygen will be to that of nitrogen as 33.8 to 29.5 (the proportions by weight in nitrous gas, according to this view of its composition) or as 7.5 to rather more than 6.5, which last number would denote the weight of the atom of nitrogen. I have, however, expressed my coincidence in the opinion, that nitrous gas consists of one atom of nitrogen and two of oxygen; which would make the weight of the atom of nitrogen  $6.5 \times 2 = 13$ .

(m) Nitrous gas and chlorine, when both perfectly dry, have no action whatsoever on each other; but, if water be present, there is an immediate decomposition, and nitrous and muriatic acids are

formed.

(n) Nitrous gas is absorbed by the green sulphate and muriate of iron,\* which do not absorb nitrogen gas. To ascertain, therefore, how much nitrogen gas a given quantity of nitrous gas contains. let it be agitated in a graduated tube with one of these solutions. This analysis is necessary, previously to deducing, from its effects on atmospheric air, the proportion of oxygen gas; for we must subtract from the residuum the quantity of nitrogen introduced by the nitrous gas.

From the important use which is now made in eudiometry of this solution of nitrous gas in sulphate of iron, it may be proper to

describe the mode of its preparation.

Dissolve as much of the green sulphate of iron in water as the water will take up, or dissolve iron filings in sulphuric acid, diluted with five or six parts of water, leaving an excess of the iron, in order to ensure the perfect saturation of the acid. Fill a wide-mouthed bottle with this solution, invert it in a cupful of the same, and into the inverted bottle receive the nitrous gas, as it is generated by the proper materials, shaking the inverted bottle frequently. The colour of this solution will change to black, and the production of gas and the agitation are to be continued, till the absorption can be carried no farther. The impregnated solution should

<sup>\*</sup> For an account of these salts, see chap. xviii. sect. 6.

be preserved in a number of small bottles, not holding more than an ounce or two each. The most commodious method of applying this solution, is by means of Dr. Hope's eudiometer, already de-

scribed. (Chap. v. sect. 4.)

(o) A very interesting experiment, affording a synthetic proof of the constitution of nitrous gas, was made by the Rev. Dr. Milner, of Cambridge.\* Into an earthen tube, about 20 inches long and three fourths of an inch wide, open at both ends, put as much coarsely powdered manganese as is sufficient nearly to fill it. Let this be placed, horizontally, in a furnace, having two openings opposite to each other, (fig. 40.) To one end of the earthen tube adapt a retort, containing a strong solution in water of pure ammonia, and to the other a bent glass tube, which may terminate in a two-necked empty bottle. To the other neck of the bottle, lute a glass tube, bent so as to convey any gas that may be produced, under the shelf of the pneumatic trough. Let a fire be kindled in the furnace; and, when the manganese may be supposed to be red-hot, drive over it the vapour of the ammonia. The alkali will be decomposed; its hydrogen, uniting with part of the oxygen which is combined with the manganese, will form water; while its nitrogen, uniting with another portion of the oxygen, will constitute nitrous gas. gas, thus generated, may be collected by the usual apparatus.

(h) Another fact, showing the mutual relation of ammonia and of the compounds of nitrogen, was discovered some years ago by Mr. Wm. Higgins.† Moisten some powdered tin (which is sold under this name by the druggists) with strong nitric acid; and, when the red fumes have ceased to arise, add some quick-lime or solution of pure potash. A strong smell of ammonia will be imme-

diately produced.

In this experiment, the tin, at the same instant, attracts the oxygen both of the nitric acid and of the water. Hydrogen and nitrogen are consequently set at liberty; and, before they have assumed the gaseous state, these two bases combine, and constitute ammonia. The ammonia, thus generated, unites with a portion of undecomposed nitric acid; and is disengaged from this combination by potash or lime, which render it evident to the smell.

#### SECTION III.

Gaseous Oxide of Nitrogen .- Nitrous Oxide of Davy.

I. This compound, also consisting of oxygen and nitrogen, but in different proportions from those of nitrous gas, may be obtained by several processes.

\* Phil. Trans. 1789.

<sup>†</sup> See his Comparative View of the Phlogistic and Antiphlogistic Theories, 2d. edition, p. 300, note.

(a) By exposing common nitrous gas for a few days to iron filings, or to various other bodies strongly attracting oxygen, this

gas is changed into the nitrous oxide.

Some nicety and experience are required to suspend the decomposition before it has gone too far; in which case nitrogen gas is obtained. The sulphate of potash, being incapable of decomposing nitrous oxide, is best adapted to the conversion of nitrous gas into that elastic fluid. The process, in all cases, may be suspended, when about two thirds the original bulk of the gas are left.

(b) By dissolving zinc, or tin, in nitric acid, diluted with five or six times its weight of water. Zinc, during this solution, disengages nitrous oxide till the acid begins to exhibit a brownish colour, when the process must be suspended, as nitrous gas is then formed. But by neither of these processes is the gas obtained sufficiently pure for exhibiting its qualities. To procure it in a state of purity the

following process is the best adapted.

(c) To nitric acid, diluted with five or six parts of water, add carbonate of ammonia, till the acid is saturated. Then evaporate the solution by a gentle heat; and, to supply the waste of alkali, add, occasionally, a little more of the carbonate. The salt obtained, after the solution has cooled, is next to be put into a glass retort, and distilled with a sand-heat, not exceeding 440° Fahrenheit.\* The heat of an Argand's lamp is more than sufficient, and requires cautious regulation. The salt will presently liquefy, and must be kept gently simmering, avoiding violent ebullition. The gas may be collected over water, and allowed to stand a few hours before it is used, during which time it will deposit a white substance, and will become perfectly transparent.

A gazometer is best adapted for its reception; because all danger is then avoided of an absorption of the water of the trough into the retort; and because the gas is brought into contact with a much smaller surface of water, which has the property of absorbing a considerable proportion of the gas. On this account, water, which has been once used to confine the gas, may be kept for the same

purpose.

The changes that take place, during the conversion of nitrate of ammonia into nitrous oxide, are the following: Nitric acid is composed of oxygen and nitrous gas; ammonia, of hydrogen and nitrogen. In a high temperature, the nitrous gas combines with an additional dose of nitrogen, and forms nitrous oxide; while the oxygen of the decomposed nitric acid unites with the hydrogen of the ammonia, and forms water. Water and nitrous oxide are, therefore, the only possible results of the decomposition of nitrate of ammonia by heat.

The gas, thus obtained, was termed, by the Society of Dutch

<sup>\*</sup> From the observations of Mr. Sadler (Nicholson's Journal, xv. 236,) it appears that the purity of the nitrate of ammonia is of considerable importance; and that its adulteration with muriate diminishes the quantity, and impairs the quality of the gas.

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Chemists, gaseous oxide of azote; but, for the sake of brevity, and as more conformable to the nomenclature of other compounds of nitrogen, I shall use, with Sir H. Davy, the name of nitrous oxide.\*

In order to ascertain whether nitrous oxide be adulterated with either common air or oxygen gas, we may mix equal measures of the gas under examination, and of nitrous gas. If any diminution ensue, the presence of one of these may be suspected; and the amount will show which of them is contained in it. Nitrous gas, however, is a much more common contamination; for it is generated, along with nitrous oxide, whenever the temperature of the salt is raised too high. Its presence may be detected either by a diminution on the admixture of oxygen gas; or by an absorption being effected, on agitating the gas with a solution of green sulphate of iron, which has no action on pure nitrous oxide.

II. Nitrous oxide gas has the following properties:

(a) It is considerably heavier than common air. At about 55° Fahrenheit and 30 inches pressure, 100 cubic inches weigh 50.20 grains, or under the same pressure, and at 60° Fahrenheit 49.68. (Davy.) More recently Sir H. Davy has stated 100 cubic inches to weigh between 48 and 49 grains, and hence its specific gravity is very nearly 1.6. Colin makes it only 1.5204, or, corrected by calculation, 1.5209. On the theory that it is constituted of one volume of nitrogen, and half a volume of oxygen, 100 cubic inches should weigh 46½ grains.†

(b) A candle burns in it with a brilliant flame and crackling noise. Before its extinction, the white inner flame becomes sur-

sounded with an exterior blue one.

(c) Phosphorus, introduced into it in a state of inflammation.

burns with increased splendour.

Phosphorus, however, may be melted and sublimed in this gas, without alteration. It may even be touched with red hot iron wire, without being inflamed; but when a wire intensely heated, or made white hot, is applied, the phosphorus burns, or rather detonates, with prodigious violence.

(d) Sulphur, introduced into nitrous oxide when burning with a feeble blue flame, is instantly extinguished; but when in a state of an active inflammation, it burns with a vivid and beautiful rose-

coloured flame.

(e) Red hot charcoal burns in it more brilliantly than in the atmosphere. When the experiment is made in a proper apparatus, the results of its combustion are found to be one measure of nitrogen gas and half a measure of carbonic acid (equivalent to half a measure of oxygen) from each measure of nitrous oxide. It must, therefore, consist of 59 parts by weight of nitrogen and 33.8 oxygen, or it must contain by weight

† Dalton, Thomson's Annals, ix. 190.

<sup>\*</sup>For a full account of this gas, consult Sir H. Davy's Researches, Chemical and Philosophical. London. Johnson, 1809.

<sup>†</sup> Two hundred cubic inches of nitrogen gas weigh 59 grains, and 100 of oxygen weigh 33.8.

Oxygen	÷	•		36.43	100	57.
Nitrogen	•	•	•	63.57	174	100.
				100.	274	157.

On the supposition that nitrous oxide is constituted of one atom of nitrogen and one of oxygen, this would make the weight of the atom of nitrogen = 13.4; for as 33.8 to 59, so is 7.5 to 13.4.

(f) Iron wire burns in this gas with much the same appearance

as in oxygen gas, but for a shorter period.

- (g) Nitrous oxide is rapidly absorbed by water that has been previously boiled, about one thirtieth the original bulk of the gas remaining uncondensed. A quantity of gas, equal to considerably more than nine-tenths the bulk of the water, may be thus made to disappear. This property furnishes a good test of the purity of nitrous oxide; for the pure gas is almost entirely absorbed by boiled water, which has cooled without the access of air. The gas employed should exceed the water three or four times in bulk, in order to obtain a saturated solution.
- (h) Water, that has been saturated with this gas, gives it out again, unchanged, when heated.
- (i) The impregnated water does not change blue vegetable colours.
- (k) It has a distinctly sweet taste, and a faint but agreeable odour.
  (l) Nitrous oxide is not diminished by admixture with either oxygen or nitrous gas.

(m) A mixture of this gas with hydrogen gas detonates loudly,

on applying a lighted taper, or passing an electric spark.

When the proportion of hydrogen is nearly equal to that of nitrous oxide, or as 39 to 40, nitrogen gas only remains after the explosion; but when the proportion of hydrogen is smaller, nitric acid is also generated. In general terms, it may be stated that one measure requires one measure of hydrogen gas, and leaves after combustion one measure of nitrogen. Nitrous oxide forms, also (as I have shown, Philosophical Transactions, 1809, page 444,) a combustible mixture with ammoniacal gas, 100 measures of the latter requiring for saturation 130 measures of nitrous oxide.

(n) Nitrous oxide is not absorbed by alkalies; but if it be brought into contact with them, when in a nascent state, or before it has assumed the form of gas, it then enters into combination with alkaline bases. Thus, when a mixture of sulphite of potash and pure potash is exposed to nitrous gas, the gas is disoxygenized by the sulphite, and changed into nitrous oxide, which unites with the alkali. We obtain, therefore, a mixture of sulphate of potash with a compound of nitrous oxide and alkali, the former of which may be separated by priority of crystallization. The latter is composed of about three parts of alkali, and one of nitrous oxide. It is soluble in water, has a caustic taste, of peculiar pungency; and converts vegetable blues to green. Powdered charcoal, mingled with

it, and inflamed, burns with bright scintillations. The nitrous oxide is expelled from fixed alkalies by all acids, even by the carbonic.

(o) Animals, when wholly confined in this gas, die speedily.

(n) One of the most extraordinary properties of this gas is exhibited by its action on the human body, when received into the lungs. When thus employed, it does not prove fatal, because, when received into the lungs, it is mixed and diluted with the atmospherical air present in that organ. To administer the gas, it may be introduced into an oiled silk bag or clean bladder, furnished with a stop-cock, and may be breathed repeatedly from the bag and back again, as long as it will last. The sensations that are produced vary greatly in persons of different constitutions; but, in general, they are highly pleasurable, and resemble those attendant on the pleasant period of intoxication. Great exhilaration, an irresistible propensity to laughter, a rapid flow of vivid ideas, and an unusual fitness for muscular exertion, are the ordinary feelings it produces. These pleasant sensations, it must be added, are not succeeded, like those accompanying the grosser elevation from fermented liquors, by any subsequent depression of nervous energy.

### SECTION IV.

#### Nitrous Acid.

Ir has been a subject of controversy whether an acid, entitled to this denomination, and holding the same relation to the nitric, which the sulphurous bears to the sulphuric, has really existence. That the acid, obtained from nitre, has different states of oxygenation, and contains a less quantity of oxygen in proportion to the depth of its colour, is generally admitted. But it has been contended that we are to consider all these varieties as nitric acid, holding in combination variable proportions of nitrous gas; and the principal argument in favour of this theory is that the substance, occasioning the colour, may be separated by the mere application of heat. Sir H. Davy, in the year 1800, gave the following table, showing the proportion of nitrous gas in nitrous acid of different colours.

100 parts by weight contain

-					\\						
Pale yellow.				Sp. Gr. 1.502	Real Acid. 90.5	Nit. Gas. 1.2	Water.				
Bright ditto					88.94	2.96	8.1				
Dark orange		•	•	1.480	86.84	5.56	7.6				
Light olive .	•	•		1.479	86.	6.45	7.55				
Dark olive .		•		1.478	85.4	7.1	7.50				
Bright green					84.8	7.76	7.44				
Blue green		•	•	1.475	84.6	8.	7.40				

Mere dilution with water is sufficient to vary these colours. Thus the dark orange-coloured acid, by dilution, passes through the shades of blue, olive, and bright green. Nitric acid, also, by absorbing nitrous gas, has its specific gravity diminished. Colourless acid, for example, when rendered of pale yellow, becomes lighter in the proportion of 1.51 to 1.502.

It is now, however, generally admitted that the nitrous acid is as much a distinct and peculiar compound as any other of the

compounds of nitrogen.

The proportions of its elements have been investigated by Sir H. Davy,\* who finds that two measures of nitrous gas and one of oxygen, (= 1 volume of nitrogen and 2 of oxygen), both freed from moisture, and mixed together in a vessel previously exhausted of air, are condensed into half their volume,† and form a deep orange-coloured elastic fluid, which may be called nitrous acid

gas. It has the following properties:

A taper burns in it with considerable brilliancy. Sulphur inflamed does not burn in it; but phosphorus burns vividly. Charcoal continues to burn in it with a dull red light. Water absorbs it and gains a tint of green. It reddens litmus paper, has a sour taste, a strong smell, and turns animal substances yellow. One hundred cubic inches, calculating from the condensation of its elements assumed by Davy, must weigh 65.3 grains, at mean temperature and pressure, and it must contain in 100 grains,

Nitrogen		•		٠	٠	30.32		100
Oxygen	•	•.	•	•	•	69.68	•	230

100.

To form liquid nitrous acid, nothing more is necessary than to saturate water with this vapour. The water becomes first green, then blue, and finally an orange colour more or less deep. The latter may be brought to the state of green or blue by adding more or less water. Hence the colour depends merely on the circumstance of density.

The properties of liquid nitrous acid, Berzelius remarks, differ from those of nitric acid; for while the latter boils at 236°, nitrous acid of the same density boils at 160°. The purely acid part he considers to be composed of 36.9 nitrogen + 63.1 oxygen. With bases, it forms a class of salts, which, he asserts, differ entirely from those containing nitric acid. On the other hand, we have the testimony of Gay Lussac that the nitrous acid is decomposed with so much facility by contact with alkaline solutions, as to be inca-

<sup>\*</sup> Elements of Chem. Philosophy.

<sup>†</sup> Gay Lussac states the condensation at two thirds of the volume of the mixture. Ann. de Chim. et Phys. i. 403.

<sup>‡ 13</sup> Ann. de Chim. 10.

pable of forming a distinct class of salts. With solution of potash, for example, he found that it affords pernitrate and nitrate, but nothing that can properly be called a nitrate of potash.\*

#### SECTION V.

## Of Per-nitrous Acid.

When 400 measures of nitrous gas and 100 measures of oxygen (in which the nitrogen and oxygen are to each other by measure as 100 to 150) are mixed together over a solution of potash confined by mercury, we obtain 100 measures of a compound, called by Gay Lussac her-nitrous acid.† Mr. Dalton, who obtained it several years ago, and then considered it as nitrous acid, has lately proposed to call it sub-nitrous acid;‡ but the name suggested by Gay Lussac seems to me more conformable to analogy, since the new acid differs from nitrous acid in containing an additional proportion of nitrogen. This new compound is so far hypothetical, that it has never yet been exhibited in a separate form; for when a stronger acid is added, to expel it from the potash, it is resolved into nitrous gas and nitrous acid.

Per-nitrous acid is, also, frequently generated, when nitrous and oxygen gases, or nitrous gas and common air, are mingled together in eudiometrical processes. At the same time nitrous and nitric acids are produced in proportions to the per-nitrous and to each other, which are modified by the circumstances of the experiment.

Calculating from the proportions of its elements and their state of condensation, 100 cubic inches of per-nitrous acid gas must weigh 80.2 grains; and it must consist in 100 grains of

Per-nitrous acid unites with sulphuric acid, either concentrated or a little diluted, and, at a moderate temperature, the compound forms elongated four-sided prisms. These crystals, and even the liquid in which they are formed, give nitrous gas when brought into contact with water. A similar solid is obtained by passing nitrous acid vapour into sulphuric acid; and it appears, also, to be identical with the crystalline solid formed by Clément and Desormes by the mixture of oxygen gas, sulphurous acid, nitrous gas,

<sup>\*</sup> Ann. de Chim. et Phys. i. 409.

Thomson's Annals, vol. ix.

<sup>†</sup> lbid. i. 400.

Dalton, Thomson's Annals, x. 83.

and the vapour of water. The last-mentioned compound had been supposed to consist of nitrous gas and sulphuric acid; but sufficient reasons have been given by Gay Lussac for the new view of it, which has just been stated.

### SECTION VI.

#### Nitrates.

### ART. 1 .- Nitrate of Potash.

I. A direct synthetic proof of the composition of this salt may be obtained by saturating nitric acid with potash, either pure or in a carbonated state. The solution, on evaporation, yields crystals

For the purposes of experiment, however, the nitrate of potash,

of nitrate of potash, or nitre.

which may be met with in the shops, and which is an abundant product of nature, may be employed on account of its greater cheapness. The nitre, which is met with as an article of commerce, is brought to this country, chiefly from the East Indies. When it arrives it is a very impure salt, containing, besides other substances, a considerable proportion of muriate of soda. In this state it is called rough nitre. For the purposes of chemistry, it requires to be purified by solution in water and re-crystallization; and it then obtains the name of refined nitre, or refined saltpetre.

II. This salt has the following properties:

(a) It crystallizes in prismatic octahedrons, generally constituting six-sided prisms, terminated by two-sided summits. It contains, according to Berzelius, no water of crystallization. Thenard has determined that it consists of

49.5 potash 50.5 nitric acid.

But as potash itself, in the driest form under which we can procure it, still contains water, Berthollet has given the following proportions as those of nitrate of potash:

50.1 potash 49.9 acid

100.\*

These proportions are nearly reversed by Berard, who makes it consist of 48.64 base and 51.36 acid.† The proportions, deduced by Dr. Wollaston, are 46.67 base to 53.33 acid: and those by Dr. Ure 47 base and 53 acid.

<sup>\*</sup> Mem. d'Arcueil, iii. 170.

(b) For solution, it requires seven times its weight of water at 60° of Fahrenheit; and boiling water takes up its own weight. This is the degree of solubility assigned by Bergman; but La Grange asserts, that, at the ordinary temperature, nitrate of potash requires only three or four times its weight of water for solution; and half its weight of boiling water.\*

(c) By the application of a moderate heat it fuses, and being east in moulds, forms what is called Sal Prunelle. After fusion, Sir H. Davy found that it still yielded water, when distilled with

boracic acid.

(d) If a red-heat be applied, nitrate of potash is decomposed in consequence of the destruction of its acid. By distilling it in an earthen retort, or in a gun-barrel, oxygen gas may be obtained in great abundance, one pound of nitre yielding about 12,000 cubic inches, of sufficient purity for common experiments, but not for purposes of accuracy.

(e) Nitrate of potash, that has been made red-hot, seems to contain an acid less oxygenated than the common nitric acid, and having a weaker affinity for alkalies. For if acetic acid be poured on nitre that has been thus treated, the nitrous acid is expelled in red fumes, whereas common nitre is not at all affected by acetic

acid.

(f) Nitrate of potash is rapidly decomposed by charcoal in a high temperature. This may be shown, by mixing two parts of powdered nitre with one of powdered charcoal, and setting fire to the mixture in an iron vessel under a chimney. The products of this combustion, which may be collected by a proper apparatus, are carbonic acid and nitrogen gases. Part of the carbonic acid also remains attached to the residuary alkali, and may be obtained from it on adding a stronger acid.

This residue was termed, by the old chemists, clyssus of nitre.

- (g) Nitrate of potash is also decomposed by sulphur, and with different results according to the temperature and proportions employed.
- 1. Mix powdered nitre and sulphur, and throw the mixture, by a little at a time, into a red-hot crucible. The sulphur will unite with the oxygen of the nitric acid, and form sulphuric acid; which, combining with the potash, will afford sulphate of potash. The production of the latter salt will be proved by dissolving the mass remaining in the crucible and crystallizing it, when a salt will be obtained exhibiting the characters described, chap. xii. sect. 4.
- 2. Mix a portion of sulphur with one sixth or one eighth its weight of nitrate of potash; put the mixture into a tin cup, and raise it, by a proper stand (fig. 25,) a few inches above the surface of water, contained in a flat shallow dish. Set fire to the mixture, and cover it with a bell-shaped receiver. In this case, also, sulphuric acid will be formed; but it will not combine, as before, with the

alkali of the nitre, which alkali is present in sufficient quantity to absorb only a part of the acid produced. The greater part of the acid will be condensed on the inner surface of the glass bell, and by the water, which will thus become intensely acid. tion may be repeated three or four times, using the same portion of water. When the water is partly expelled, by evaporation in a glass dish, concentrated sulphuric acid remains, which has been formed by the union of the oxygen of the nitre, and that of the atmospherical air, with the sulphur submitted to experiment. By a a process of this kind, conducted on a large scale, and in extensive leaden chambers, the sulphuric acid of commerce is prepared. The dilute acid, resulting from the union of the condensed vapour of the burning materials, with the stratum of water at the bottom of the chamber, is first boiled down in part in shallow leaden vessels, and is then transferred into glass retorts, where it is farther concentrated by the continued application of heat.

In a memoir of Clément and Desormes, published in Nicholson's Journal, xvii. 41, it is proved, that the nitre does not furnish above one tenth part of the oxygen, required for the conversion of sulphur into sulphuric acid, and that the rest of the oxygen is derived from the atmospherical air of the chamber. Sulphurous acid, they suppose, is in the first instance formed by the combustion of the sulphur; and, at the same moment, nitrous gas is evolved from the de-oxygenation of the nitric acid contained in the saltpetre. This nitrous gas, uniting with the atmospheric oxygen, composes nitrous acid gas, which, when water is present, has the property of converting sulphurous into sulphuric acid, and of returning, at the same time, to the state of nitrous gas. The same process is repeated, and thus the same portion of nitrous gas acts repeatedly as an intermedium between the sulphur, previously changed into sul-

phurous acid, and the atmospheric oxygen.

(h) A mixture of three parts of powdered nitre, two of carbonate of potash, or common salt of tartar, and one part of sulphur, all accurately mixed together, forms the *fulminating powder*, which explodes with a loud noise, when laid on an iron heated below redness.

(i) A mixture of five parts of powdered nitre, one part of sulphur, and one of powdered charcoal, composes gunpowder. The materials are first very finely powdered separately, then mixed up together, and beaten with a wooden pestle, a sufficient quantity of water being added to prevent an explosion. The mixture is afterward granulated, by passing through sieves, and dried very cautiously.\*

## Process for preparing Nitric Acid.

Nitrate of potash is decomposed by sulphuric acid, which combines with the potash, and expels the nitric acid. Put into a glass

<sup>\*</sup> On the preparation of gunpowder, and the theory of its detonation, consult Nicholson's Journal, xxiii. 277.

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retort, which may be either tubulated or not, four parts of nitrate of potash, reduced to a coarse powder, and pour upon it three parts of concentrated sulphuric acid. Apply a tubulated receiver, of large capacity, between which, and the retort, an adopter may be interposed; these junctures being luted with a mixture of pipeclay, sifted sand, and cut tow or flax. To the tubulure of the receiver, a glass tube may be fixed by means of the fat lute, and may terminate in another large receiver, containing a small quantity of water.

If the operator wishes to collect the gaseous products also, this second receiver should be provided with a tubulure, to which a bent pipe may be luted, terminating under one of the inverted funnels in the shelf of the pneumatic trough. Apply heat to the retort, through the intervention of a sand-bath. The first product that passes into the receiver, is generally of a red colour, and of a smoking quality. These appearances gradually diminish; and if the materials used were clean, the acid will come over pale, and even colourless. Afterwards it gradually re-assumes a red colour, and smoking property; which appearances go on increasing till the end of the operation; and the whole product, mingled together, has either a yellow or an orange colour, according to the temperature employed.

The proportions recommended in the new London Pharmacopæia for the preparation of nitric acid are two pounds of nitrate of potash, deprived by heat of its water of crystallization, and two pounds of sulphuric acid. These are directed to be mixed in a glass retort, and distilled in a sand-bath, until a red vapour arises. The acid in the receiver is to be mixed with an ounce of nitrate of potash, and again distilled in a similar manner. After the second distillation its specific gravity is 1.500; and one fluid-ounce, Mr. Phillips finds, decomposes 476 grains of marble. But he objects to the proportion of sulphuric acid, in the process of the College, as unnecessarily large. If, however, it be required to decompose the whole of any portion of nitre, it is necessary to use as much sulphuric acid, as will form, with the alkali of the nitre, super sulphate of potash, viz. 97 parts of acid, of density 1.85, to 100 parts of nitre.

The nitric acid which first passes over, has the greatest specific gravity. In an experiment of Dr. Perceval of Dublin, the product was taken in three portions; the first of which had the specific gravity of 1.494, the second of 1.485, and the third of 1.442.\* Gay Lussac, by two successive distillations of nitric acid of specific gravity 1.3 from four times its weight of sulphuric acid, brought it to the density of 1.610. In this state, he found it to be decomposed by heat or light with extraordinary facility.†

In the large way, and for purposes of the arts, it is usual to substitute earthen or cast iron retorts, made extremely thick, for those of glass. An earthen head is adapted, and this is connected with

<sup>\*</sup> Trans. of the Irish Academy, iv. 37. † Ann. de Chim. et Phys. vol. i.

a range of proper condensors. The strength of the acid is varied also, by putting more or less water into the receiver. What is called double aqua fortis varies in its specific gravity from 1.3 to 1.4.

Nitric acid, obtained by this process, is never perfectly pure. It contains, generally, both sulphuric and muriatic acids; the former of which is indicated by a white precipitate, on adding a solution of nitrate of barytes to a little of the acid, diluted with 8 or 10 parts of water; and the latter, by a milkiness produced by nitrate of silver. The sulphuric acid may be separated, either by a second distillation from a portion of very pure nitre, equal in weight to one eighth of that originally employed, or by adding nitrate of barytes; allowing the precipitate to settle; decanting the clear liquid, and distilling it. Muriatic acid is separated by the addition of nitrate of silver. An immediate milkiness ensues, and fresh additions must be made to nitrate of silver, as long as it occasions this appearance. Then allow the precipitate to subside; decant the clear liquid, and re-distil it; leaving one eighth or one tenth in the retort. The product will be pure nitric acid. Nitrate of lead may be substituted for nitrate of silver.\* The nitric acid may also be obtained free from muriatic acid, if a perfectly pure nitrate of potash be employed for distillation. This purification is effected by repeated solutions of the nitre, in boiling distilled water, and re-crystallizations.

Nitric acid obtained in this manner is deficient also in another respect, for it is not perfectly oxygenated, but holds in solution a considerable quantity of nitrous acid. To expel the latter, put the acid into a retort, to which a receiver is applied, the two vessels not being luted, but joined merely by paper. Apply a very gentle heat for several hours to the retort, changing the receiver as soon as it becomes filled with red vapours. The nitrous gas will thus be expelled, and the acid will remain in the retort in a state of purity, and as limpid and colourless as water. It must be kept in

a bottle secluded from the light.

One hundred parts of nitrate of potash, according to La Grange, yield by this process 43 of acid, or, according to my experience, above 50; but, if the process of the College be followed, 100 of fused nitre afford about 66½ of acid. Even this, however, is not the whole of what was contained in the salt; for a part is decomposed by the temperature necessary to the operation. Accordingly, a large quantity of oxygen gas is disengaged during the distillation, and may be collected by an obvious addition to the apparatus.

In the retort, there remains a compound of potash with more sulphuric acid than is essential to its saturation, or a super-sulphate of potash. On submitting this to a pretty strong heat, the excess of sulphuric acid is expelled; and the residue, dissolved and eva-

porated, affords crystallized sulphate of potash.

<sup>\*</sup> See Nicholson's Journal, xi. 134.

### ART. 2 .- Nitrate of Soda.

I. This salt may be formed, by saturating carbonate of soda with nitric acid; or by distilling common salt with three fourths of its weight of nitric acid. When the former process is adopted, the solution must be evaporated, till a pellicle appears on its surface, and then allowed to cool. Crystals will be produced, having

the shape of rhomboids, or rhomboidal prisms.

II. These crystals have a taste like that of saltpetre, but more intense. They are soluble in three parts of water at 60°, and in less than an equal weight of boiling water. They attract moisture from the atmosphere. In other respects, in the means by which their decomposition is effected and its results, they agree with the nitrate of potash. The only use of nitrate of soda is, perhaps, that which has been suggested by Proust, who has found it to be more economical in the making of fire-works than nitrate of potash.\* It consists, according to Dalton, of

57.6 acid 42.4 base

100:

### ART. 3.—Nitrate of Ammonia.

I. The most simple mode of preparing this salt is by adding carbonate of ammonia to dilute nitric acid, till saturation has taken place. If the liquor be evaporated, by a heat between 70° and 100°, to a certain extent, it shoots, on cooling, into crystals, having the shape of six-sided prisms, terminated by long six-sided pyramids. Evaporated at a temperature of 212°, it yields, on cooling, thin fibrous crystals; and when the evaporation is carried so far, that the salt immediately concretes on a glass rod by cooling, it then forms a compact and shapeless mass.

II. The solubility of this salt varies, according to the temperature in which it has been formed. When in crystals, it requires twice its weight of water, for solution, or half its weight of boiling water. It deliquiates, in all its forms, when exposed to the atmos-

phere.

III. The most important property of this salt is the one which has been already described, viz. of yielding, when decomposed by heat, the nitrous oxide. One pound of the compact kind gives, by careful decomposition, nearly five cubic feet of gas, or rather more than 34 doses; so that the expense, estimating the salt at 5s. 10d. the pound, is about 2d. for each dose.

IV. In a temperature of 600° this salt explodes, and is entirely decomposed. Hence it was formerly called nitrum flammans.

<sup>\*</sup> Nicholson's Journal, xv. 262. See also 6 Ann. de Chim. et Phys. 206.

V. Its composition varies according to the mode of its preparation, and is stated by Sir H. Davy as follows:

Prismati					
69.5		72.5		74.5	acid
18.4		19.3		19.8	ammonia
					water
100.		100.		100.	

The prismatic variety is stated by Berzelius,\* who investigated very carefully the results of its decomposition, to consist of

67.625 acid-21.143 base 11.232 water

### ART. 4 .- Nitrate of Barytes.

Nitrate of barytes may be prepared, by dissolving either the artificial or native carbonate in nitric acid, diluted with eight or ten parts of water. If the artificial carbonate be employed, it should be previously well washed with distilled water, till the washings cease to precipitate nitrate of silver. A solution of nitrate of barytes, mixed with one of silver, should continue perfectly transparent. On evaporation, it yields regular octahedrons, often adhering to each other in the form of stars; and sometimes it is obtained in small brilliant plates. It requires for solution 12 times its weight of water at 60°, and three or four parts of boiling water. It is not altered by exposure to the air. In a red heat its acid is decomposed, and the earth remains pure. This furnishes another method of procuring pure barytes; but the heat must not be carried too far, otherwise the barytes is apt to vitrify with the cruci-The residue, on the addition of water, dissolves with great heat and noise, and the solution, on cooling, yields crystals of pure barytes.

Nitrate of barvtes is composed, in 100 parts, according to Clément and Desormes, of 60 base, and 40 acid and water. Mr. James Thomson states its composition to be

59.3 barytes
40.7 acid and water.

This scarcely differs from the determination of Berzelius, viz. 58.46 base + 41.54 acid, and no water.

<sup>\*80</sup> Ann. de Chim. 182.

#### ART. 5 .- Nitrate of Strontites.

This salt may be obtained in the same manner as the nitrate of barytes, with which it agrees in most properties. The solubility of its crystals, however, differs considerably; for they are dissolved by their own weight of water at 60°, or by little more than half their weight of boiling water. When applied to the wick of a candle, or added to boiling alcohol, they communicate to the flame a deep blood-red colour. They are decomposed by a high temperature, and afford pure strontitic earth. Exclusive of water, the salt consists, according to Richter, of 51.4 acid + 48.6 base; or, according to Stroméyer, of 50.62 acid + 49.38 base.

#### ART. 6 .- Nitrate of Lime.

This salt is found abundantly in the cement of old buildings, which have been long inhabited. To prepare it artificially, nitric acid, diluted with five or six parts of water, may be saturated with carbonate of lime, 63 parts of which are decomposed by 90.23 of nitric acid of density 1.5, and give 103.05 of dry nitrate of lime.\* When this solution is boiled down to the consistence of syrup, and exposed in a cool place, long prismatic crystals are formed, resembling, in their disposition, bundles of needles diverging from a common centre. These crystals are readily soluble in water, of which, at 60°, they require two parts, and boiling water dissolves an equal weight. They deliquiate speedily, when exposed to the air; and are decomposed at the temperature of ignition. Exclusive of water, it contains,

				Acid.	Base.
According to Dalton				61.3	38.7
					34.4

When a solution of nitrate of lime is evaporated to dryness in an earthen vessel, then fused for five or ten minutes in a crucible, and poured, while in fusion, into an iron pot previously heated, the congealed mass forms Baldwin's phosphorus. It must be broken into pieces, and preserved in a well-stopped phial. These pieces, after having been exposed to the sun for a few hours, emit in the dark a beautiful white light, affording one variety of solar phosphorus.

## ART. 7.—Nitrate of Magnesia.

This compound may be prepared, by dissolving carbonate of magnesia in diluted nitric acid. The solution, when evaporated, yields crystals in the shape of prisms, with four oblique faces truncated at their summits. Most commonly, however, it forms a shapeless mass, consisting of an immense number of small needle-

<sup>\*</sup>Phillips, Journal of Science, v. 167.

shaped crystals, crossing each other irregularly. These crystals deliquiate in the air, and are soluble in half their weight of water. When exposed to the heat of ignition, they fuse; a few bubbles of oxygen gas first escape; and the nitric acid then passes undecomposed. The salt contains, exclusive of water, according to Dalton, 69 acid + 31 base.

## ART. 8.—Nitrate of Alumine.

This salt is but little known. It may be formed by the solution of fresh precipitated alumine, which has been well washed with distilled water, but not dried in diluted nitric acid, with the assistance of heat. The solution, which has always an excess of acid, after evaporation, crystallizes in thin ductile plates. The crystals are extremely soluble; and, on the application of a high temperature, abandon their acid. They are decomposed by most alkalies and earths. Pure potash, added in excess, re-dissolves the precipitate.

### ART. 9 .- Nitrate of Glucine.

The nitrate of glucine is a sweet tasted salt, which cannot be brought to crystallize. When evaporated to dryness, it rapidly absorbs moisture from the atmosphere. It is soluble in alcohol. A high temperature decomposes it, without effecting its previous fusion.

## ART. 10 .- Nitrate of Zircon

The nitric acid dissolves, but cannot be saturated with, fresh precipitated zircon. The solution has always an excess of acid. When evaporated, it forms a yellowish transparent mass, extremely tenacious and viscid, and difficultly dried. It has a styptic astringent taste, and leaves on the tongue a thick substance, in consequence of its partial decomposition by the saliva. This dry nitrate is extremely soluble. The solution is decomposed by sulphuric acid, and by carbonate of ammonia, which throw down a precipitate soluble in an excess of the acid, or of the carbonate. Tincture of galls forms a white precipitate, which is soluble in an excess of the tincture.

## ART. 11 .- Nitrate of Yttria

May be prepared by dissolving yttria in nitric acid. The solution has a sweetish astringent taste; and, in most properties resembles nitrate of glucine. It can scarcely be obtained in crystals; and if too great a heat be applied during evaporation, the salt becomes soft, assumes the appearance of honey, and concretes on cooling, into a hard stony mass. Exposed to the air, it attracts moisture, and is resolved into a liquid.

#### SECTION VII.

### Nitrites.

THE easiest mode of obtaining the salts, which by some have been considered as nitrites, is to deprive the acid, contained in the nitrates, of part of its oxygen, by exposure for a short time to the temperature of ignition. This method, it must be obvious, cannot be used with those nitrates that abandon their acid on the application of heat, or which, like nitrate of ammonia, are completely decomposed.

Nitrate of potash, after ignition in a crucible, emits, when powdered, a smell of nitrous gas. When diluted nitric acid, or even acetic acid, is poured upon it, vapours of nitrous acid are disengaged; and hence it appears, that the affinity of this acid for its base is weakened by partial dis-oxygenation; for no such effect arises on adding these acids to the nitrate. The solution of the salt in water changes the syrup of violets to green. Its other properties are little known.

It has, however, been already stated in the section on nitrous acid, that the existence of such a class of salts as the nitrites is extremely questionable.

## CHAPTER XIV.

MURIATIC ACID—OXYMURIATIC ACID OR CHLORINE—AND THEIR COMPOUNDS.

THERE are few subjects, respecting which the opinions of chemists have undergone such frequent changes, as concerning the nature of chlorine. The view originally taken by Scheele, the illustrious discoverer of this substance, was, that the muriatic acid is a compound of a certain base and an imaginary principle called phlogiston: and that by the action of certain bodies, it becomes dephlogisticated, or deprived of that supposed principle of inflammability.\* It was afterwards found, however, that all bodies, which are capable of producing this change in muriatic acid, contain oxygen, and that their proportion of oxygen is diminished by the process. It appeared, therefore, to be an obvious conclusion, that what takes place in the action of metallic oxides on muriatic acid is simply the transference of oxygen from the oxide to the muriatic acid; and conformably with this theory, the resulting gas received the name of oxy-muriatic acid. Sir H. Davy was led, by his earlier experiments, to modify, in some degree, this view of the theory of the operation; and to consider the muriatic acid as a compound of a certain basis with water, and the

<sup>\*</sup> On Manganese, § xxiii. xxiv.

oxy-muriatic as a compound of the same basis with oxygen. modification was rendered necessary by the fact, that when a metallic oxide is heated in muriatic acid gas, oxymuriatic acid is obtained, and water appears in a separate state; it was evident, therefore, that muriatic acid gas must either contain water ready formed; or the elements of water; or hydrogen, capable of composing water with the oxygen of the oxide. But, at a subsequent period, that distinguished philosopher was induced, by the experiments of Gay Lussac and Thenard, as well as by his own, to form a different theory on the subject. Oxy-muriatic acid, he now considers as a simple or undecompounded substance; and muriatic acid, as a compound of that simple substance with hydrogen. To convert the muriatic acid into chlorine, we have only, according to this view, to abstract hydrogen from the muriatic acid; and this, it is supposed, is all that is effected by the action of those oxides, which are adapted to the purpose. Again, to convert chlorine into muriatic acid, we have only to supply it with hydrogen; and accordingly the simple mixture of one measure of each of those gases, when exposed for a short time to the sun's rays, or exploded by an electric spark, affords two measures of muriatic acid gas.

The oxy-muriatic acid or chlorine (as Sir H. Davy proposes to call it, in order to avoid all connection of its name with hypothetical views) is supposed, also, to unite at once with the metals, without requiring, like the sulphuric or nitric acid, that the metals should first be in the state of oxides. In proof of this theory, it appears to be sufficiently established, that no oxygen can be obtained either alone, or in combination with combustible bodies added for the purpose, from the compounds of chlorine and metals. The analyses, however, of the metallic muriates, as they were formerly considered, remain unimpeached by this change of theory. All that is necessary, to transmute in idea a muriate into a compound of chlorine, is to deduct the oxygen from the metallic oxide; and, adding it to the muriatic acid, to consider the sum as chlorine. For example, muriate of soda, deprived of all water, consists

On the ole Soda com	l theory, posed of	of m	uris {( {}	itic Oxy Sod	ac ger iun	id n i	••	19 40	3.5 3.5	. 46 } 54
•										100
On the new	theory it	cons	ieta	οf		•				,
Sodium			•	•						40.5
Chlorine,	46+13.5	==	•	.•	•	•	٠	•	•	59.5
										100.

It is remarkable that there is hardly any fact, connected with the chemical history of chlorine and muriatic acid, that does not admit of being equally well explained upon the hypothesis that chlorine is a Vol. 1.—T t

compound, as upon that of its being a simple substance. On the whole, however, the probabilities certainly appear to me very much in favour of the new, or rather the revived opinion of its elementary nature; especially since the discovery of iodine. But there are still objections to its implicit adoption, which this is not the proper occasion to state. I shall only observe, that not the least important of these objections is, the instantaneous conversion, which the theory of chlorine supposes, of the metallic combinations of that body into muriates, when they are dissolved in water, the oxygen of which is imagined to pass, in a moment, to the metal, while the hydrogen is attracted by the chlorine. In the present state of the inquiry, indeed, we stand in need of some fact, which will admit of explanation only on one of the opposed theories; and shall serve the purpose of an experimentum crucis.

#### SECTION I.

### Compound of Chlorine with Hydrogen.

CHLORINE unites with hydrogen either silently or with detonation,

accordingly as the experiment is conducted.

1. Let a phial, provided with a well-ground stopper, be completely filled with a mixture of hydrogen and chlorine gases in exactly equal bulks. Put the stopper into its place, and keep the bottle, twenty-four hours, inverted with its mouth under water. On withdrawing the stopper under water, nearly the whole of the gas will have disappeared: and the remainder will be absorbed by the contact of the water.

2. Mingle, in the detonating tube (fig. 28 or 29,) equal volumes of hydrogen and chlorine gases. When an electric spark is passed through the mixture, a detonation will ensue, and nearly the whole will be absorbed. But if the gases have been carefully dried by exposure to solid muriate of lime, their volume, after firing, will not be at all condensed, and muriatic acid gas, precisely equal to their joint bulk, will be obtained. By weight, one part of hydrogen gas requires 33.5 of chlorine gas for saturation, and 34.5 of muriatic acid gas are produced.

The result of this experiment may either be explained, by admitting the direct combination of hydrogen and chlorine to constitute muriatic acid; or by supposing that the hydrogen unites with the oxygen of the oxy-muriatic acid, and that the water, thus formed, exists as an element of muriatic acid gas. In this instance, the theory of

chlorine has certainly the advantage in point of simplicity.

If the weight of the atom of chlorine be determined from its union with hydrogen, it will be expressed by 33.5; and 33.5 of chlorine will be the equivalent to 7.5 of oxygen. When oxygen is made the decimal unit, as by Dr. Wollaston, the weight of the atom of chlorine will be expressed by 44.1, or in round numbers by 44. On the sup-

position that the oxy-muriatic acid is a compound of muriatic acid and oxygen, it must be constituted as follows:

Oxygen Muriatic acid	·	22.65 77.35	•	•	100. 341.5	:	•	29.2 100.	8
				-		1	-	<del></del> -	_
	•	100.			441.5			129.2	8

This would indicate the weight of the atom of muriatic acid to be nearly 26; and adding an atom of oxygen, the compound atom of

oxy-muriatic acid would still weigh 33.5.

A remarkable fact, respecting the mutual action of oxy-muriatic acid and hydrogen gases, was discovered by Gay Lussac, and, without any knowledge of his experiments, by Mr. Dalton. A mixture of the two gases, in equal volumes, is slowly condensed under ordinary circumstances; but if the direct rays of the sun happen to fall on the mixture, the two gases diminish with considerable rapidity; and, if the quantity be large, they even explode. This is a striking instance of the agency of light in promoting chemical union. Blue light is more effective in producing the condensation than red, but neither occasions the rapid combustion, which is excited by the direct rays of the sun.\* It is probable, that in this case, the combination is favoured by increase of temperature, which was ascertained by Sir H. Davy to augment the combustibility of mixtures of oxygen and hydrogen gases. According to Grotthus, a mixture of chlorine and hydrogen ceases to explode by electricity when rarefied six times, but Sir H. Davy found it to be still explosive when rarefied no less than 24 times.

#### Muriatic Acid Gas and its Solution in Water.

I. The muriatic acid, in its purest form, exists in the state of a gas, which is permanent over mercury only. For exhibiting its properties,

therefore, a mercurial apparatus is absolutely necessary.

To obtain muriatic acid gas by a more easy method than the direct union of chlorine and hydrogen gases, let the tubulated gas bottle (plate ii. fig. 17) be about one-fourth, or one-third, filled with well dried muriate of soda (common salt) in lumps, not in powder. To this adapt the acid-holder, filled with concentrated sulphuric acid; and let the aperture of the bent pipe terminate under a jar filled with, and inverted in, quicksilver. Open the communication between the acid and the salt, by turning the cock; and immediately on the contact of these two bodies, an immense quantity of muriatic acid gas will be disengaged. A common or tubulated gas bottle, or tubulated retort, will answer sufficiently well for procuring the gas. The first portions, that come over, may be allowed to escape under a chimney; because they are contaminated by the admixture of common air present in the bottle. The subsequent portions may be preserved for use; and the pure gas will exhibit the following qualities:

<sup>\*</sup> Seebeck, 34 Nicholson's Journal, p. 220.

(a) It has a very pungent smell; and is sufficiently caustic to blister the skin, when applied to it for some time.

(b) When brought into contact with common air, it occasions a white cloud. This is owing to its union with aqueous vapour, which

is always present in the atmosphere.

(c) It extinguishes a lighted candle. Before the flame goes out, the upper part of it assumes a greenish hue, the cause of which has not yet been explained. A white vapour also surrounds the extinguished wick, owing to the combination of water, produced by the combustion of the candle, with the muriatic acid gas.

(d) It is heavier than common air. Gay Lussac states its specific gravity at 1.278, and hence 100 cubic inches weigh, as nearly as possible, 39 grains; according to Sir H. Davy, between 39 and 40. Biot and Arago make its specific gravity, by experiment, 1.2474, or, by

calculation, 1.2505.

(e) It effects the liquefaction of a piece of ice, almost as rapidly as

it would be melted by a red-hot iron.

(f) It is very rapidly absorbed by water. A drop or two of water, admitted to a large jar full of this gas, causes the whole of it instantly to disappear. According to Mr. Kirwan, an ounce-measure troy of water absorbs 800 cubical inches (i. e. 421 times its bulk) of muriatic acid gas; and the water, by this absorption, is increased about one-third its original volume. Dr. Thomson's experiments indicate a still larger absorption, viz. 515 cubical inches, or 308 grains by one cubic inch, equal to 252 grains, of water, at 60° Fahrenheit; the barometer standing at 29.4. Berthollet has shown that 100 grains of water absorb 12.467 grains of muriatic acid gas deprived of all redundant water by passing it through a tube surrounded by a freezing mixture. By this absorption, we obtain an acid of the specific gravity 1061.4; and hence it follows that acid of this density contains, in 100 grains,

only 8.55 of real acid.

(g) When potassium is introduced into muriatic acid gas, dried by contact with fused muriate of lime, it immediately becomes covered with a white crust; it heats spontaneously; and, by the assistance of a lamp, acquires, in some parts, the temperature of ignition, but does not inflame. If the potassium and the gas be in proper proportions, they both entirely disappear; a white salt is formed, and a quantity of pure hydrogen gas is evolved, which is equal to rather more than one-third the original volume of the acid gas. Eight grains of potassium, in an experiment of Sir H. Davy, effected the absorption of nearly twenty-two cubic inches of muriatic acid gas; and the quantity of hydrogen gas produced amounted to more than eight cubical inches. It is remarkable that potassium, by its action on muriatic acid gas, separates exactly the same quantity of hydrogen, as would result from its agency on water. This has been considered as a proof, that the evolved hydrogen has its origin from water, which the gas is supposed to hold in combination. But the phenomena are equally well explained by admitting, that muriatic acid is decomposed by the potassium, which seizes the chlorine, and sets the hydrogen at liberty. And on the corpuscular theory of Mr. Dalton, whether potassium act on water or on muriatic acid, in each case an atom of hydrogen will be disengaged; since the metal must attract to itself

either an atom of oxygen or of chlorine.

Various expedients were tried, by Sir H. Davy, to obtain muriatic gas from perfectly dry materials, with the view to determine, whether potassium is capable of detaching hydrogen from gas so prepared. But it was found that materials, which when moist are capable of affording muriatic acid, yield no gas whatsoever, when in a perfectly dry state. None, for example, could be obtained by strongly heating a mixture of dry phosphoric or boracic acid with dry muriate of lime. This fact would appear, on first view, favourable to the opinion, that water is essential to the constitution of muriatic acid gas. But it is equally consistent with the theory of chlorine; for, according to that theory, no compound of chlorine and a metallic base can yield muriatic acid, till hydrogen is supplied with which the chlorine may unite. If muriatic acid gas contained water as an essential element, it might be expected that water should be separated by the action of certain metals on the gas itself, or on muriate of ammonia; and though experiments in proof of this have been advanced by Dr. Murray and Dr. Ure,\* yet, on repeating those experiments, sources of fallacy have been discovered by Sir H. Davy, which had escaped their authors; and the moisture has been traced to the union of oxygen derived from unsuspected sources with the hydrogen of the muriatic acid-

(h) When muriatic acid gas is electrified in contact only with glass, by means of an apparatus which I have described in the Phil. Trans. for 1812, chlorine and hydrogen gases are found, after the experiment, in quantity never exceeding 1-35th the original bulk of the gas. This result may either be explained by supposing that the water of muriatic acid gas is decomposed, and that the oxygen unites with the acid, while the hydrogen is liberated; or it may be accounted for on the new theory, which requires nothing more than the separation of the chlorine and hydrogen, constituting muriatic acid, by the agency of the electric fluid. They cannot, however, exist together in a greater proportion than 1-35th to the whole mixture, without reuniting and reforming muriatic acid. When the experiment is made over mercury, the chlorine combines with that metal, and a mixture of muriatic acid and hydrogen gases remains, from which water ab-

sorbs the former, leaving the hydrogen pure.

(i) When muriatic acid gas and oxygen gases are electrified together, oxy-muriatic acid is formed, directly, as the old theory would explain, by the union of the acid with oxygen; or, as the theory of chlorine teaches, the oxygen unites with the hydrogen of muriatic

acid gas, and merely liberates chlorine.

(k) Muriatic acid gas and nitrous acid have no action on each other, and are incapable of forming aqua regia. But when colourless nitric acid and muriatic gas dissolved by water are brought into contact, the hydrogen of the muriatic acid, according to Sir H. Davy, detaches the oxygen of the nitric acid, and the chlorine of the former

<sup>\*</sup> Edin. Trans. † P

acid is developed. On the old theory, this fact may be explained by supposing the attraction of muriatic acid insufficient to take oxygen from nitrous acid; but that it has the power of attracting that quantity of oxygen which constitutes the difference between nitrous and nitric acids. The former view, however, it must be admitted, is the more simple and perspicuous.

(1) When a small piece of barytes or strontites, obtained by the decomposition of the nitrate, and therefore free from water, is heated by means of a spirit lamp, in a retort filled with muriatic acid gas, the gas is first dilated, and is then rapidly absorbed. The barytes or strontites becomes red-hot, and the compound, which is produced, runs into fusion.\* At the close of the experiment, a sensible quantity of water is condensed. This water may either have pre-existed in the muriatic acid gas, or it may have been formed, by the union of the hydrogen of the acid, with the oxygen of the barytes or strontites which has been employed. Under the latter view, we are to consider the solid product as a compound of chlorine with barium or strontium.

### Process for preparing Liquid Muriatic Acid.

Into a tubulated retort, placed in a sand-bath, put eight parts of dried muriate of soda; and, to the tubulure, lute the bent tube (fig. 26, a) with fat lute. To the neck of the retort, affix a tubulated receiver (fig. 30, b) by means of the same lute; and to the aperture of this adapt a tube, twice bent at right angles, and furnished with Welter's contrivance for preventing absorption (fig. 31, b,) the longer leg of which terminates beneath the surface of water contained in a twonecked bottle. From the other neck, let a second right-angled pipe proceed; and this may terminate in a similar manner, in a second bottle containing water; the total quantity of which, in all the bottles, may be about five parts. Let the junctures be all carefully luted; and, when they are sufficiently hardened, pour very gradually through the bent tube five and a half parts by weight of strong sulphuric acid, making the additions at several distant intervals. On each affusion of the acid a large quantity of muriatic acid gas will be liberated, and will be absorbed by the water of the first bottle, till this has become saturated. It will then pass on to the second bottle, and be there absorbed. The water employed may amount to half the weight of the salt, and may be equally distributed between the two bottles. These it is better to surround with cold water, or, still preferably, with ice or snow; because the condensation of the gas evolves considerable heat, which prevents the water from attaining its full impregnation. When the whole of the sulphuric acid has been added, and the gas no longer issues, let a fire be lighted in the furnace, beneath the sand-bath, removing the bent tube a, and substituting a well-ground glass stopper. This will renew the production of gas; and the temperature must be preserved, as long as gas continues to be evolved. At this period it is necessary to keep the luting, which

Chevreul, 84 Ann. de Chim. 285.

connects the retort and the receiver, perfectly cool; otherwise it will be apt to melt. To this juncture, indeed, I prefer the application of the clay and sand lute; but to apply this properly requires a little practice. Towards the close of the process, a dark-coloured liquid is condensed in the first receiver, consisting of a mixture of sulphuric and muriatic acids. When nothing more comes over, the operation may be suspended, and the liquid in the two bottles must be preserved in bottles with ground stoppers. It consists of liquid muriatic acid.

The liquid muriatic acid may also be obtained by diluting the sulphuric acid with the water necessary for the condensation of the gas, and adding the dilute acid, when cold, to the salt in the retort. To the retort, an adopter may be luted with the clay and sand lute; and this may terminate in a large tubulated receiver, from the aperture of which a right-angled Welter's tube is conveyed beneath a few ounces of water, contained in a two-necked bottle. A fire must then be lighted under the sand-bath, and continued as long as any liquor comes over. The adopter and receiver must be kept cool, by the constant application of moistened cloths.

The proportions, directed by the London College of Physicians, in their Pharmacoposia of 1809, are those recommended by Vauquelin, viz. four parts of dried salt, three of sulphuric acid, and three of water, of which last one-third is to be employed in diluting the acid, and two-thirds to be put into the receiver. Mr. R. Phillips, however, finds that the water and acid are in unnecessary excess; and that the most economical proportions are 32 parts of salt, and 21.9 (say 22) of sulphuric acid, of density 1.850, which may be diluted with one-third its weight of water, the remaining two-thirds being placed, as before, in the receiver.\* The weight of the acid produced should equal, or a little exceed, that of the salt employed.

If the muriatic acid, thus obtained, should contain sulphuric acid, which may be discovered by muriate of barytes occasioning a white precipitate, the acid is to be re-distilled from a fresh portion of muriate of soda. When prepared by Woulfe's apparatus, the product in the second bottle is always perfectly pure.

The acid, formed by the process of the College, has the specific gravity only of about 1.142; that of commerce is generally about 1.156; but by Woulfe's apparatus, and especially when the bottles are surrounded by ice or snow, it approaches 1.500. A fluid ounce of the specific gravity 1.142 dissolves 204 grains of marble; and the same quantity of sp. gr. 1.174 decomposes 240 grains. The intermediate degree of specific gravity, however, which has been mentioned (viz. 1.156 or thereabouts), is best adapted for keeping; for the denser acid emits a large quantity of fumes, which are extremely inconvenient and injurious to all metallic instruments.

The caput mortuum consists of sulphate of soda with some undecomposed muriate of soda. The former may be obtained, in a crystallized form, by first driving off, by a strong heat, the excess of sulphuric acid that adheres to it; and then dissolving in hot water. The

<sup>\*</sup> On the London Pharmacop. p. 10.

product of sulphate of soda exceeds that of the muriate employed in the proportion of about eight to five.

- Liquid muriatic acid has the following properties:

  1. It emits white suffocating fumes. These consist of muriatic acid gas, which becomes visible by contact with the moisture of the
- 2. When heated in a retort, or gas bottle, muriatic acid gas is disengaged, and may be collected over mercury.

3. Liquid muriatic acid is not decomposed by the contact of char-

coal, essential oils, or other combustible bodies.

4. When diluted with water, an elevation of temperature is produced, much less remarkable, however, than that occasioned by diluting sulphuric acid; and when the mixture has cooled to its former temperature, a diminution of volume is found to have ensued. The capacity of the diluted acid for heat Dr. Ure has found to be less than the mean capacity of the strong acid and of water, which sufficiently accounts for the increased temperature.\*

5. In a perfectly pure state liquid muriatic acid is quite colourless; but it has frequently a yellowish hue. This may proceed, either from a portion of chlorine, or of muriate of iron, but most commonly of the latter. This colour is instantly destroyed by a few drops of muriate of tin; but this addition, instead of diminishing, increases the

impurity of the acid.

6. Muriatic acid combines readily with alkalies, and with most of

the earths, both in their pure and carbonated states.

7. Liquid muriatic acid is specifically heavier than water. The correspondence between its specific gravity, and the quantity of real acid, which it contains, is shown by the following Table, given by Sir H. Davy in his Elements of Chemical Philosophy. It is constructed from experiments made with great care by Mr. E. Davy in the Laboratory of the Royal Institution.

Table showing the Quantity of real Acid in Liquid Muriatic Acid of different Specific Gravities. (Temp. 45° Faht. Barom. 30.)

Specific gravity.	100 grains contain of Muriatic Acid Gas.	Specific gravity.	100 grains contain of Muriatic Acid Gas.
1.21	42.43	1.10	20.20
1.20	40.80	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.95	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.06
1.13	26.26	1.02	4.04
1.12	24.24 22.3	1.01	2.02

Thomson's Annals, x. 273.

The proportion of dry or real muriatic acid, in liquid acid of different densities, has also been investigated by Dr. Ure, who has ascertained that acid of density 1.192 contains in 100 parts by weight 28.3 of real muriatic acid; and has given some general formulæ for deducing the proportion of real acid in liquid acid of various specific gravities.\* The table, deduced from his experiments, will be found in the Appendix at the end of the second volume.

### SECTION II.

Compound of Chlorine with Oxygen, viz. Oxides of Chlorine; Chloric Acid, and Per-chloric Acid.

When chlorate or hyper-oxymuriate of potash (a salt which will be afterwards described) is distilled, at a gentle heat, with weak muriatic acid, a gas may be collected over mercury, which is found to differ essentially from chlorine. Its colour has a dense tint of brilliant yellow green; and its smell resembles that of burnt sugar, mixed with the peculiar smell of chlorine. Water seems to take up eight or ten times its volume, and acquires an orange tint. It has been called by its discoverer, Sir H. Davy, Euchloric gas, or simply Euchlorine. Gay Lussac has proposed for it the name of oxide of chlorine; but it may, with more propriety, be called Protoxide of Chlorine.

Euchlorine explodes by a gentle heat, applied to the vessel which contains it, and five parts in volume become six, consisting of a mixture of oxygen and chlorine gases, in such proportions that euchlorine must be composed of two in volume of chlorine and one of oxygen, the latter being condensed into half its bulk, or by weight of

Chlorine										
Oxygen .	•	•	•	٠	18.56	•	•	•	•	22.79

100.

These proportions indicate that euchlorine is constituted of one atom of chlorine 33.5 + one atom of oxygen 7.5, and hence its atom must weigh 41.

When detonated with twice its volume of hydrogen gas, there is a condensation of more than two-thirds of the mixture, and liquid

muriatic acid is formed.

Mercury has no action on euchlorine at common temperatures. Antimony and copper burn in it, if introduced previously heated. Sulphur and phosphorus decompose it; and charcoal already ignited burns in it with a dull red light. Nitrous gas condenses it with red fumes.

Thomson's Annals, x. 369.

Euchlorine destroys vegetable colours; but it first gives the blue a tint of red.

In almost all cases of vivid combustion, there is a condensation of the bodies which unite; but in the decomposition of euchlorine by heat, we have the remarkable phenomenon of an explosion, accompanied with heat and light, and an expansion of the elements, which are separated from each other.

### Per-oxide of Chlorine,

Another compound of chlorine and oxygen, containing a larger proportion than euchlorine, of the latter element, has been discovered by Sir H. Davy,\* and has since been made the subject of a series of experiments by Count Stadion of Vienna.† As it exhibits no acid

properties, it may be called per-oxide of chlorine.

To procure it, 50 or 60 grains of the powdered chlorate or hyper-oxymuriate of potash, are to be mixed with a small quantity of concentrated sulphuric acid. When thoroughly incorporated, a solid mass will result, of a bright orange colour. This is to be introduced into a small retort of glass, which is to be exposed to the heat of water gradually warmed, but prevented from attaining the boiling point, by an admixture of spirit of wine. Count Stadion obtained it by fusing a small quantity of chlorate (hyper-oxymuriate) of potash, in a retort. Over this, when cool, he poured concentrated sulphuric acid, and exposed the retort to water for three hours, gradually raising its temperature to 212°. The gas may be received over mercury, on which it has no action at common temperatures.

It has a lively yellow colour, much more brilliant than that of euchlorine; is much more rapidly absorbed by water; and has a peculiar aromatic smell, not mixed with any smell of chlorine. According to Davy, it destroys vegetable blue colours, without first reddening them; but Count Stadion asserts that it does not change blue paper. When heated to about the temperature of 212° Faht., or, according to Count Stadion, to between 112° and 144°, it explodes with more violence, and a greater expansion of volume, than euchlorine, producing much light. After explosion over mercury, from 2.7 to 2.9 volumes appear, for every two of gas decomposed; and, of these, two, as Count Stadion, also, admits, are oxygen and the rest chlorine. A little chlorine is absorbed, however, by the mercury, and it is reasonable, Sir H. Davy thinks, to conclude that the deep vellow gas is, in reality, composed of two in volume of oxygen, and one of chlorine, condensed into two volumes. If this be correct, the gas will consist, by weight, of one atom of chlorine 33.5, and four atoms of oxygen 30, and its atom will weigh 63.5. But if, as Stadion asserts, it gives two volumes of chlorine and three of oxygen, it should consist of one atom of chlorine and only three of oxygen.

It is decomposed, at common temperatures, by no combustible

Phil. Trans. 1815, Part II.

<sup>†</sup> Thomson's Annals, ix. 22.

body, except phosphorus, which occasions an explosion when introduced into it, and burns, in the liberated gases, with great brilliancy.

Its saturated solution in water, which contains seven volumes of gas, is of a deep yellow colour. It does not taste sour, but extremely astringent and corroding; and it leaves on the tongue a disagreeable and lasting impression. The solution may be kept in the dark unchanged, but when exposed to the sun's rays it is decomposed, and chlorine and chloric acid are obtained.

#### Chloric Acid.

A third compound of chlorine and oxygen was pointed out by Mr. Chenevix, some time before it was obtained in a separate form, as existing in the class of salts called hyper-oxymuriates. For the method of exhibiting it in a distinct state, we are indebted to Vauquelin\* and Gay Lussac.† The following is the process: To a solution of pure chlorate of barytes (the mode of preparing which will be described in art. 4. sect. 4), add by degrees dilute sulphuric acid, as long as it occasions any precipitation. This separates the barytes, and leaves the chloric acid combined with water only. It is important to add no more sulphuric acid than is barely sufficient; for the slightest excess renders the chloric acid impure. If the right quantity has been used, the liquid obtained should remain perfectly transparent, when, taking two separate portions of it, we add to the one dilute sulphuric acid, and to the other chlorate of barytes. If either of these agents occasions a precipitate, we must add it by degrees till the effect ceases. The clear liquid is then to be decanted by a syphon, and reserved for use. It is a solution of chloric acid in water; and has the following properties:

1. It is free from colour; its taste is acid and astringent; and its smell, when concentrated and a little heated, is moderately pungent.

2. It reddens the infusion of litmus. Paper stained with litmus, though it does not immediately lose its colour, yet is deprived of it in a day or two if left in the liquid; or more rapidly if taken out of the liquid and exposed to the air, in consequence of the solution becoming more concentrated.

3. It does not precipitate either silver, mercury, or lead, from their

solution in nitric acid.

4. It is volatilized by heat, but not without a partial decomposition into chlorine and oxygen. Hence it afterwards precipitates the nitrate

of silver.

5. Muriatic acid decomposes it, and both acids, if mixed in just proportion, are changed entirely into chlorine. On the old theory, part of the oxygen of the chloric acid passes to the muriatic acid, and oxygenates it. On the new theory of chlorine, the oxygen of the chloric acid unites with the hydrogen of the muriatic acid, and the chlorine, pre-existing in both, is thus developed.

<sup>\*</sup> Ann. de Chim. xcv. 102.

<sup>†</sup> Ibid. xci. 111.

6. Chloric acid is decomposed, also, by sulphuretted hydrogen and by sulphurous acid. In the first case, chlorine and sulphur are separated, and water is formed. In the second, sulphuric acid is formed, and chlorine set at liberty. None of the acids, which are saturated with oxygen have any action on chloric acid.

7. All the metals that are capable of decomposing water, decompose also the chloric acid, and afford compounds of chlorine with a

metallic oxide.

According to the experiments of Vauquelin, chloric acid is composed of

Chlorine Oxygen							
		-	100				

This determination differs materially from that of Gay Lussac, according to whom 32.304 oxygen convert 28.924 chlorine into chloric acid, and hence it should be composed of

Chlorine			٠.		47.3				100			•	90
Oxygen	•	•	•	•	52.7	•	•	•	110	•	•	•	100
					100.								

The result of Gay Lussac is by much the more probable of the two, and would make the chloric consist of 1 atom of chlorine + 5 atoms of oxygen, while Vauquelin's numbers would indicate no less than 8 atoms of oxygen. Mr. Chenevix formerly stated the composition of the hyper-oxymuriatic or chloric acid to be 65 oxygen + 35 muriatic acid. To accommodate this view to the new theory, 10.4 taken from the oxygen and added to the muriatic acid will give 45.4 and 54.6, numbers not very different from those of Gay Lussac.

It is proper, however, to add that the existence of a simple combination of chlorine and oxygen has been denied by Sir H. Davy, who considers the liquid, obtained by Gay Lussac, as constituted of two proportions (atoms) of hydrogen, one of chlorine and six of oxygen. To this, the latter has replied, that the hydrogen is not an element of the acid itself, but of water with which the acid is united, as is the case with liquid sulphuric and nitric acids. The reader, who takes an interest in this controversy, may find it in the first volume of Annales de Chimie et de Physique, and of the Journal of Science and the Arts; and the argument for the existence of hydrogen in certain acids as an essential and acidifying principle, and not as a constituent of water, has, also, been ably supported by Dr. Murray, in a late volume of the Edinburgh Transactions.

## Per-chloric Acid.

In obtaining peroxide of chlorine by Sir H. Davy's or by Count Stadion's process, a peculiar salt is formed, which was first noticed

by the latter philosopher. It is mixed with bisulphate of potash, which may be separated by a second crystallization, and the peculiar salt then appears in octohedral crystals. It requires 55 times its weight of water at 60° for solution, but dissolves freely in boiling water. In alcohol it is quite insoluble. When distilled with an equal weight of sulphuric acid, at a temperature of 280° Faht it is decomposed: and an acid (of whose properties, however, we have not a distinct account) may be distilled over. When the salt is distilled alone at 412°, it is converted into chloride of potassium (dry muriate of potash) and oxygen gas, in the following proportions. One hundred parts by weight afford

Hence it appears that 25.59 chlorine are united with 45.92 oxygen, which is nearly in the proportion of 33.5 chlorine to 58 oxygen. Now to have agreed with the proportion of seven atoms of oxygen, the last mentioned number should have been 52.5; and if we suppose the oxygen a little over-rated, which may very probably be the case in a compound so imperfectly investigated, the per-chloric acid will then consist of one atom of chlorine = 33.5, united with seven atoms of oxygen = 52.5; and the weight of its atom will be 86.

#### SECTION III.

## Chlorine with Nitrogen.

CHLORINE has no action whatsoever on nitrogen gas, nor on nitrous gas or nitrous oxide, when both gases are perfectly dry; but a compound of chlorine and nitrogen may be formed, by passing chlorine gas through a solution of nitrate of ammonia, or of almost any ammoniacal salt, of the temperature of 40° to 50° Fahrenheit. The chlorine gas is rapidly absorbed, and a film appears on the surface, which soon collects into yellowish drops, that sink to the bottom of the liquor.

This yellowish and oily fluid is the most powerfully detonating compound with which we are acquainted. When gently warmed, it explodes with so much violence, that it is not safe to employ a quantity larger than a grain of mustard seed. Its discoverer, M. Dulong,\* was severely wounded in his first experiments on this substance; and Sir H. Davy had a serious injury done to his eyes in repeating them. It is expedient, therefore, to proceed with great caution.

<sup>\*</sup> See Ann. de Chim. vol. 85.

When a globule of this fluid is thrown into olive oil, turpentine, or naphtha, it explodes even without heat, and so violently, as to shatter any glass vessel. The same effect ensues, when it touches phosphorus, or phosphorized alcohol or ether; but pure alcohol seems to deprive it of its explosive property, and renders it a white oily matter. The specific gravity of the fluid, Sir H. Davy has determined to be 1.653, water being 1. It is not congealed, by exposure to the cold produced by snow and muriate of lime.

The products of its detonation are chlorine and nitrogen gases, but it is impossible to determine the bulk of those elements which are afforded by a given weight. The best method of analyzing it, is by its action on mercury, which unites with the chlorine, and sets the nitrogen free. From various experiments of this kind, Sir H. Davy concludes that it is composed of four in volume of chlorine to one in

volume of nitrogen, or of

	•	•	•	•	•	91.2
Nitrogen	•	•	•	•	•	8.8
•						100.

These proportions correspond best with the opinion, that it is constituted of one atom of nitrogen to two atoms of chlorine; but the coincidence is not so exact, as in the case of some other compounds,

and the analysis requires confirmation.

Chlorine and nitrous gases, separately dried by solid muriate of lime, do not combine on admixture; but when moisture is present, the chlorine decomposes water, forming muriatic acid with its hydrogen, while its oxygen condenses the nitrous gas.

### SECTION IV.

Chlorine with the Metals of the Alkalies and Earths, and with the 'Oxides of those Metals.

When potassium is heated in chlorine gas, it burns much more vividly than in oxygen; each grain absorbs 1.1 cubic inch of the gas, and a neutral compound is formed, precisely resembling that which results from heating potassium in dry muriatic acid gas. Sodium burns in chlorine with similar appearances, and condenses twice as much of the gas, as is absorbed by an equal weight of potassium.

When potassium or sodium, which have been made to absorb oxygen, are heated in chlorine gas, the latter disappears, and oxygen gas, precisely equivalent to what had been condensed, is liberated. Oxygen is expelled, also, by chlorine, from barytes, strontites, and lime, in the proportion of one measure for every two measures of chlorine that are condensed.

As the oxygen is always evolved in its original quantity, though the quantity of chlorine absorbed is variable, Sir H. Davy considers this as proving that the oxygen does not proceed from the chlorine, but from the oxide; and that chlorine is a simple body, which attracts the metals in question more strongly than oxygen attracts them.

Ammonia is decomposed by chlorine, sometimes with detonation. If both gases are dry, no water is produced, which Sir H. Davy observes should happen, if chlorine contained oxygen; but the products are muriatic acid (from the union of the chlorine and hydrogen,) and nitrogen gas.\* The muriatic acid, with the undecomposed alkali, forms muriate of ammonia.

#### SECTION V.

Chlorine with Charcoal, Carbonic Oxide, and Carburetted Hydrogen.

When the charcoal of beech wood, finely powdered and perfectly dry, is poured into chlorine gas in its ordinary state, an inflammation ensues. But charcoal, intensely ignited by the strongest powers of Voltaic electricity, in dry chlorine gas, effects no change, nor is any

carbonic acid produced.†

Perfectly dry chlorine and light carburetted hydrogen gases, in the experiments of Dr. John Davy, detonated without producing carbonic acid. Muriatic acid gas was formed, and the charcoal was precipitated. But when the gases are fired over water, carbonic acid is obtained, the oxygen for which is furnished by the water. Mixtures of three or four parts of chlorine and one part of carburetted hydrogen over water, when exposed to the light of the sun, explode, and carbonic acid is generated; or, if the quantities are small, and indirect light only is admitted, the action of the gases goes on slowly, with similar results.

When three measures of chlorine are mixed with two and a half of olefiant gas or per-carburetted hydrogen, a white cloud appears, and, if the gases are pure, the whole is rapidly condensed. At the same time, a liquid resembling oil is formed, which has a greater specific gravity than water. From this property, per-carburetted hydrogen first received the name of olefiant gas; but it has been lately shown that the liquid obtained is analogous, not to oil but to ether, whence it has been called chloric ether. It will be described under that name

in the second volume.

The condensation of per-carburetted hydrogen by chlorine gas affords an easy way of estimating the quantity of the former, in any mixture of it with hydrogen, light carburetted hydrogen, and carbonic oxide gases. Add to any gas, suspected to contain olefant gas, about half its bulk of chlorine; if an immediate diminution ensue, accompanied with an evident production of an oily liquid, the presence of

<sup>\*</sup> Phil. Trans. 1814, p. 70. † Children. Phil. Trans. 1815, p. 369.

olefiant gas may be safely inferred. Of the whole quantity condensed, about 45 hundredths may be estimated to be per-carburetted

hydrogen.

A mixture of equal volumes of chlorine and carbonic oxide gases, both dried by fused muriate of lime, and exposed, about a quarter of an hour, to bright sunshine, affords a peculiar compound, called by its discoverer, Dr. John Davy,\* *Phosgene Gas*. The colour of the chlorine is destroyed by this combination, and the constituent gases are condensed into half their bulk. Hence it appears to be one of the heaviest gases known, 100 cubic inches being estimated to weigh 105.97 grains.

Phosgene gas has an intolerably pungent odour, and reddens litmus, whence it is called by some chemists phosgenic acid. Water changes it into muriatic and carbonic acid gases. The metals decompose it, and unite with the chlorine, a volume of carbonic oxide being liberated, equal to the bulk of the original gas. It condenses four times its volume of ammoniacal gas, and the product is a white neutral salt, from which the stronger acids disengage muriatic and carbonic acids; but acetic acid dissolves it without effervescence.

#### SECTION VI.

### Chlorine with Sulphur and its Compounds.

SULPHUR, when heated in contact with chlorine gas, absorbs it, and forms a singular compound first described by Dr. Thomson.† Ten grains absorb nearly 30 cubic inches of gas, which is nearly in the proportion of 15 (the weight of an atom of sulphur) to 33.5 (the weight of an atom of chlorine). It appears, indeed, to be a true chloride of

. sulphur.

This fluid is volatile below 200° Fahrenheit. Its colour is red by reflected light, but yellowish green by transmitted light. It emits fumes, which are peculiarly acrid, and which excite a copious flow of tears. Its specific gravity is 1.6. It decomposes water, the hydrogen of which forms, with the chlorine, muriatic acid; while the sulphur, with the oxygen of the water, composes sulphuric acid. Before dilution, however, it is not acid, and does not redden dry litmus paper.

Dry chlorine gas has no action on dry sulphurous acid gas; but if water be present, muriatic and sulphuric acids result from their

mixture.

When chlorine gas is mixed with sulphuretted hydrogen gas, the phenomena vary with the proportions. When equal bulks are used, there is scarcely any condensation, and the residue contains 19 twentieths of its bulk of muriatic acid gas. In this case sulphur is precipitated. But if enough of chlorine be used, besides the same product of muriatic acid, the sulphur is changed into chloride of sulphur.

The compound of chlorine and phosphorus will be described in

speaking of the latter substance.

Phil. Trans. 1812.

<sup>†</sup> Nicholson's Journal, 8vo. vol. vi.

#### SECTION VII.

#### Chlorine with the Metals.

Almost every metal, in a state of minute division, takes fire spontaneously, and burns in this gas. The very malleable metals, such as gold, silver, &c. which can be reduced to extremely thin leaves, are best applied to the gas in that state. Others, as iron, zinc, copper, &c. must be introduced in the state of fine filings. The most readily oxidized metals burn with the greatest brilliancy. The best proportion is about 40 grains of each metal to 40 cubic inches of gas: and, into the bottom of the receiver a little sand may be poured, to prevent it from being broken.

Metallic antimony burns with a very brilliant white flame, and throws out sparks. Arsenic exhibits a fine green or blue flame, attended with sparks, and a dense white smoke; bismuth a bluish flame; nickel, a yellowish white one; cobalt, a bluish white; zinc, a white flame and sparks; tin, a bluish white light; lead, a clear white flame; copper, a red and slowly spreading light; and iron, a bright red light. In all these experiments, the temperature of the gas

should not fall short of 70°.

When chlorine is made to act on any metallic oxide, those of iron and arsenic excepted, the whole of the oxygen is expelled from the oxide, and the chlorine combines with the metal only. The description of these compounds, which have been ably investigated by Dr. J. Davy, will form a part of the history of the individual metals in the next volume.

## Nomenclature of the Compounds of Chlorine and of Muriatic Acid.

The combinations of muriatic acid continue to be termed Muriates in the modified nomenclature, proposed by Sir H. Davy. Thus muriate of magnesia, of alumine, and of ammonia; are correct expressions. But all compounds of chlorine with combustible bases, that philosopher proposes to designate by annexing the termination ane to the Latin name of the basis. The compound of chlorine and sulphur, he calls for example, sulphurane; that of silver (argentum) and chlorine argentane; and so of the rest. Common salt, on the same principle, would be termed sodane. When these compounds are capable of uniting with an additional proportion of chlorine, he expresses that which has two proportions by the termination ana or anea. Thus copper (cuprum) with one proportion of chlorine is cuprane, and with two cupranea. This nomenclature appears, however, to have gained little acceptation among chemists.

It is more agreeable to analogy with the combinations of oxygen, to distinguish the compounds of chlorine by the name of chloride, a termination conformable to that of oxide. The different compounds of chlorine, with one base, may than be designated in the way proposed by Dr. Thomson for the oxides, the first being called proto-chloride,

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the second deuto-chloride, and so of the rest. Gay Lussac, conceiving chlorine to have a stronger analogy with sulphur and phosphorus than with oxygen, proposes for its compounds the name of chlorures; but, as, it appears to me, without sufficient reason.

It will assist the recollection of the reader, if a general view be now offered of the various compounds of chloric, and of their nomen-

clature.

I. With Hydrogen, chlorine forms only one compound, muriatic acid, for which the name of hydro-chlore or hydro-chloric acid has been proposed by the French chemists. For its compounds, they propose, instead of muriates, the epithet hydro-chlorates.

II. With Oxygen, it composes four compounds:

With one atom of chlorine to one of oxygen, protoxide of chlorine, (euchlorine of Davy.)

With one atom of chlorine to four of oxygen, peroxide of chlo-

With one atom of chlorine to five of oxygen, chloric acid. With one atom of chlorine to seven of oxygen, perchloric acid.

III. With Combustible and Metallic Bases: With Carbon . . . No combination. - Carbonic oxide Phosgene gas. --- Nitrogen . . Chloride of nitrogen. (Detonating compound of Dulong). - Sulphur . . . Chloride of Sulphur. (Fuming liquor of Thomson). 1. Protochlorides.
2. Deuto-chlorides.
3. Trito-chlorides.
4. Tetro-chlorides. With Metals

According to the views of Sir H. Davy and Gay Lussac, all the bodies described in the next section, excepting the muriates of ammonia, magnesia, and alumine, are to be considered strictly as chlorides or chlorures, that is to say, as compounds of chlorine with metallic bases. Common salt, for example, they conceive to be a compound, not of muriatic acid and soda, but of chlorine and sodium, at least in its dry state. Until these views, however, are completely established, I have deemed it unnecessary to separate bodies, so naturally allied by similarity of properties; and I shall continue therefore, to class with the muriates, some compounds, which, in the farther progress of science, will probably be removed to a different genus of salts.

#### SECTION VIII.

## Muriates (Hydro-Chlorates.)

### ART. 1.—Muriate of Potash.

MURIATE of potash may be obtained by saturating muriatic acid with carbonate of potash, and evaporating the solution till the salt crystallizes. These crystals have a cubical shape, and a bitter disagreeable taste; they dissolve in three times their weight of water at 60°, and in a rather less proportion of boiling water. They undergo little change when exposed to the air; they decrepitate when thrown on the fire, but abandon no part of their acid at a red heat.

Muriate of potash consists, in 100 grains,

According to Bertholet	•	of		Acid. 33.34			Base. 66.66
Berzelius							
——— Dr. Wollaston	. •		• •	36.57	•	•	63.43

Berzelius, by decomposing 100 grains of the fused salt with solution of nitrate of silver, obtained 192.4 of luna cornea. According to Sir H. Davy, this salt after fusion is composed of 75 parts of potassium united with 67 chlorine, or 100 grains consist of

Potassium			•					<b>52.8</b>
Chlorine :	•	•	•	•	•	•	•	47.2
								-
								100.

These proportions are almost the same as those stated by Gay Lussac, viz. 100 chlorine + 111.31 potassium, all confirming that this salt is composed of an atom of each of its ingredients. A hundred parts, it is calculated by Dr. Ure, when completely decomposed by sulphuric acid, yield 129½ of liquid muriatic acid, specific gravity, 1.192.

## ART. 2.—Muriate of Soda.

Muriate of soda is that well known substance, common salt, which is become a necessary ingredient in the food of man, and is of essential utility in several of the arts.

I. Its composition may be proved, by the direct union of soda with muriatic acid. But for purposes of experiment, the common salt may be employed, which is to be found in the shops. This may be purified, by adding to a solution of it in water a solution of carbonate of soda, as long as any milkiness ensues; filtering the solution, and evaporating it till it crystallizes.

II. Its qualities are as follow:

1. It crystallizes in regular cubes, which, when the salt is pure, are but little changed by exposure to the air. The common salt of the shops, however, acquires an increase of weight, in consequence of the absorption of moisture. The various forms under which it appears, of stoved salt, fishery salt, bay salt, &c. arise rather from modifications in the size and compactness of the grain, than from any essential difference of chemical composition.

2. It requires, for solution, twice and a half its weight of water, at 60° of Fahrenheit, and hot water takes up very little more. Hence its solution crystallizes, not like that of nitre, but by cooling, by eva-

poration.

3. When heated gradually it fuses, and forms, when cold, a solid-

compact mass.

4. If suddenly heated, as by throwing it on red-hot coals, it decrepitates. It does not, however, after being dried at the temperature of boiling water, lose by ignition more than two or three parts of water per cent. and essentially it contains no water.

5. It is not decomposed when ignited in contact with inflammable substances, except with potassium, which sets at liberty half its

weight of sodium.

When mixed with powdered charcoal or sulphur, and fused in a crucible, it does not undergo any decomposition or essential change.

- 7. It is decomposed by the carbonate of potash, the alkali of which combines with the muriatic acid of the salt, and the carbonic acid is transferred to the soda.—Hence we obtain muriate of potash and carbonate of soda. A process for effecting this decomposition, on a large scale, is described by Westrumb, in Grell's Journal, English translation, ii. 127.
- 8. It is decomposed by the sulphuric acid in the mode already described. Nitric acid also separates the muriatic acid.

9. Muriate of soda is composed, in 100 grains,

According to	Darcet		of		49.27		Base. 50.73
	Berard		 		48.		<i>57</i> .
	Dr. Mar	cet	 	•	46.		<b>54.</b>
·	Berzeliu	8 .	 		46.55		53.44

From 100 grains of transparent rock salt, dissolved in water, and precipitated by nitrate of silver, I obtained 242 of luna cornea; Dr. Marcet, from 100 grains of pure artificial muriate of soda, fused before solution, obtained 241.6; Berzelius, 244.6; and Rose, 243.4. Now 100 grains of luna cornea may be stated, in round numbers, to denote 19 grains of real muriatic acid, so that it is easy, from this datum, to calculate the composition of common salt, or of any muriatic salt, which has been decomposed by nitrate of silver.

On the atomic system of Mr. Dalton, it should consist of an atom of muriatic acid combined with an atom of soda. But according to Sir H. Davy's view, fused common salt is constituted of an atom of

sodium, weighing 22, with an atom of chlorine weighing 5.35 or of

Sodium Chlorine									
	,								
				100.			247		168

Dr. Wollaston assumes its constitution to be either 39.64 sodium + 60.36 chlorine; or on the old theory of muriatic acid, he admits its composition as stated by Berzelius. One hundred grains are estimated by Dr. Ure to be capable of yielding, when completely decomposed by sulphuric acid, 165 of liquid muriatic acid, specific gravity 1,190, or 186.3 grains of density 1.160.

## ART. S .- Muriate of Ammonia.

1. If equal measures of ammoniacal gas and muriatic acid gas be mixed together, over mercury, they are immediately and totally condensed, a white cloud is formed, and a solid substance is deposited on the sides of the vessel.—This is the muriate of ammonia. For experimental purposes it may be procured in the shops, under the name of sal-ammoniac.

Berzelius, from 100 grains, precipitated by nitrate of silver, obtained 267.87 of luna cornea. Hence he calculates its composition, independently of water, to be

But in its ordinary state the salt contains water, for when distilled with lime, the earth gains a greater increase of weight than the muriatic acid only could furnish. The proportions are, according to Berzelius,

Base	
Base 31	50
	95
Acid 49	55

These proportions differ very little from the results of Dr. Ure, who infers the dry muriatic acid in 100 parts of sal ammoniac to be 50 or 51 only\*, equivalent to 67.8 of the acid gas.

This is one of the few salts which, consistently with Sir H. Da-

<sup>\*</sup> Thomson's Annals, x. 211.

wy's views, can properly be considered as a true muriate. Its atomic constitution Mr. Dalton believes to be one atom of acid and two atoms of ammonia. The notion of its being a compound of chlorine with the imaginary substance of ammonium, or a chloride of ammonium, appears not to be tenable †.

Muriate of ammonia exhibits the following properties:

(a) It is volatilized, without being liquefied or decomposed, or in ether words may be sublimed. Sir H. Davy finds that it may even be passed, without alteration, through glass or porcelain tubes heated to redness. When, however, it is transmitted over ignited metals, it is decomposed into its gaseous elements.

(b) It is readily soluble in water, three parts and a half of which, at 60° take up one of the salt. During its solution much caloric is absorbed. In boiling water, it is still more soluble; and the solution,

on cooling, shoots into regular crystals.

(c) It slightly attracts moisture from the air.

(d) On the addition of a solution of pure potash, or pure soda, the alkali is disengaged, as is evinced by the pungent smell that arises on the mixture of these two bodies, though perfectly inodorous when separate.

(e) Though generally considered as a neutral salt, yet, if placed on litanus paper and moistened, Berzelius observes, that the paper

is reddened after some moments, as it would be by an acid.

(f) It is decomposed by barytes, strontites, lime, and magnesia.

# Process for obtaining Solution of Ammonia in Water.

The following process is given by Mr. R. Phillips, as preferable

to that of the London Pharmacopæiat.

On 9 oz. of well-burnt lime, pour half a pint of water, and when it has remained in a well closed vessel for nearly an hour, add 12 ounces of muriate of ammonia, and about 3½ pints of boiling water. When the mixture has cooled, filter the solution; and, having put it into a retort, distil off 20 fluid ounces. The solution will have the specific gravity 0.954, which is quite as strong as it can be conveniently kept. If the solution be required to be more strongly impregnated, this will be best effected, by passing ammoniacal gas through it, from a mixture of equal parts of powdered lime and muriate of ammonia, by means of an apparatus similar to that described for the preparation of muriatic acid.

When a mixture of one part of powdered muriate of ammonia with from one to two of powdered carbonate of lime (chalk), both perjectly free from moisture, is distilled together in a retort, a solid white substance condenses on the inner surface of the receiver. This is the sub-carbonate of ammonia; and the process now described is that by which, with the substitution of proper subliming vessels, the sub-carbonate of ammonia is prepared for sale. This operation furnishes an example of double affinity. The carbonic acid,

Use in Thomson's Annals, x. 211.

<sup>†</sup> Remarks on the London Pharm. p. 34.

being transferred from the lime to the ammonia, forms sub-carbonate of ammonia; and the muriatic acid, passing to the lime, composes muriate of lime.

### ART. 4.—Muriate of Barytes.

Muriate of barytes may be formed by heating pure barytes in chlorine gas, each measure of which disengages half a measure of oxygen gas from that earth. Or when barytes is heated in muriatic acid gas, the gas disappears, and the salt, which is produced, becomes redhot. But for purposes of experiment, muriate of barytes is best prepared, by dissolving either the artificial or native carbonate in muriatic acid much diluted; or, if neither of these can be had, the sulphuret. The iron and lead, which are occasionally present in the carbonate, and are dissolved, along with the barytes, may be separated by the addition of a small quantity of liquid ammonia, or by boiling and stirring the solution in contact with a little lime; or, which is still better, by solution of barytes in water. When filtered and evaporated, the solution yields regular crystals, which have most commonly the shape of tables, bevelled at the edges, or of eight-sided pyramids, applied base to base They dissolve in five parts of water, at 60°, or in a still smaller quantity of boiling water; and also in alcohol. They are not altered by exposure to the atmosphere; not are they decomposed, except partially, by a high tempe-The sulphuric acid separates the muriatic; and the salt is also decomposed by alkaline carbonates and sulphates.

Fifty grains of ignited muriate of barytes give 68 of luna cornea.

It is composed,

According to Mr. A. Ail Berzelius	kin •	, <b>.</b>	•	of —	•	•	•	26.80 26.23	5 . 3 .	•	73.14 73.77	
And the crystallized sale	co	nsis	ts		•			•				
According to Mr. Aikin				. 22			. 6		•			

Its atomic constitution, according to Mr. Dalton, is 1 atom of acid and 1 atom of base; and the crystals consist of 1 atom of dry salt and 2 atoms of water. Sir H. Davy considers the dry salt as a compound of 1 atom of barium weighing 65, and 1 atom of chlorine 33.5. Hence 100 parts should consist of

Chlorine						34.	
Barium	•	•			•		

hin A

### ART. 5 .- Muriate of Strontites

May be obtained by following the same process as that employed in preparing the barytic salt. The solution affords long slender hexagonal prisms, which are soluble in two parts of water, at 60°; and to almost any amount in boiling water. In a very moist atmosphere they deliquiate. They dissolve in alcohol, and give a blood-red colour to its flame.

Fifty grains of dry muriate of strontites give 85 of luna cornea, and hence the salt must consist of 67.5 acid. This agrees very nearly with Kirwan's determination, but differs somewhat from Vauquelin's viz. 61 base and 39 acid, Stromeyer, who has lately examined this salt, makes it consist of

According to Sir H. Davy's view, it is constituted of 29 parts strontium and 21 chlorine, or of

Strontium - - - - - 58. Chlorine - - - - 42.

Its atomic constitution, agreeably to this view, is one atom of metal weighing 45, and one atom of chlorine weighing 33.5. On the old theory, it should consist of one atom of strentites, and one atom of muriatic acid.

## ART. 6.-Muriate of Lime.

This salt may be prepared by dissolving carbonate of lime in muriatic acid, or by washing off this soluble part of the mass which remains after the distillation of the solution of pure ammonia from muriate of ammonia and lime. One hundred grains of carbonate give, according to Berzelius, 109.6 of fused muriate of lime.

The solution crystallizes in six-sided striated prisms, terminated by very sharp pyramids. If it be evaporated to the consistence of a syrup, and exposed to a temperature of 32°, it forms a compact mass, composed of bundles of needle-shaped crystals, crossing each other confusedly. The dry salt retains its acid at the temperature of ignition.

The crystals dissolve in half their weight of cold water, and to an unlimited extent in boiling water, being, in fact, soluble in their water of crystallization.—They deliquiate rapidly in the air, and enter into fusion when heated. After being melted by a strong heat, the

fused mass still contains water; for by ignition with iron filings, it yields much hydrogen gas. On the new theory of chlorine, however, this gas may proceed from the decomposition of muriatic acid. If fused in a crucible, and treated in the same manner as the nitrate of lime, the crystals yield a solar phosphorus, called, from its discoverer, *Homberg's phosphorus*. When mingled with snow, they produce intense cold, as has already been described.

Dry muriate of lime may be inferred, from an experiment of Dr.

Marcet, to consist of

One hundred grains of fused muriate of lime give, according to Davy, 250 grains of luna cornea; according to Berzelius 287.5. From experiments on its synthesis, Berzelius states its composition to be

and that of the crystallized salt

But, according to the theory of Sir H. Davy, the salt after being ignited, consists of 31 chlorine and 19 calcium, or of

## ART. 7.—Muriate of Magnesia.

This is also a deliquescent and difficultly crystallized salt. It has an intensely bitter taste; is soluble in its own weight of water, or in five parts of alcohol. Unlike the preceding muriates, it is decomposed, but not entirely by ignition.

According to Mr. Dalton, Muriate of Magnesia is constituted of 56.4 acid + 43.6 base; but from Dr. Wollaston's table of equivalents, it may be deduced to consist of 58 acid and 42 base. The

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compound of chlorine and magnesium, though supposed by Sir H. Davy to exist, has not yet been examined in a separate state. When heated, the combination, he remarks, is destroyed; the chlorine decomposes water, and escapes in the state of muriatic acid, and the oxygen of the water forms magnesia with the metal.

The muriates of magnesia and lime are generally contained in muriate of soda, and impart to that salt much of its deliquescent property. They impair, too, its power of preserving food. They are

also ingredients of sea-water.

### ART. 8 .- Muriate of Alumine

May be formed by dissolving fresh precipitated alumine in muriatic acid; but the acid is always in excess. It is scarcely possible to obtain this salt in crystals; for, by evaporation, it assumes the state of a thick jelly. It is extremely soluble in water, and deliquescent when dry. In a high temperature it abandons its acid entirely. No compound (Sir H. Davy observes) exists, that can be considered as a compound of alumine and chlorine.

## ART. 9.—Muriate of Glucine.

This salt is little known. Like all the salts of glucine, it has a sweet taste, and crystallizes more readily than the nitrate.

## ART. 10.—Muriate of Zircon.

Fresh precipitated zircon is readily dissolved by muriatic acid. The compound is colourless; has an astringent taste; and furnishes, by evaporation, small needle-shaped crystals, which lose their transparency in the air. It is very soluble in water and in alcohol. It is decomposed by heat, and by the saliva of the mouth. The gallic acid, poured into the solution, precipitates, if it be free from iron, a white powder. Carbonate of ammonia gives a precipitate, which is re-dissolved by an excess of the carbonate.

## ART. 11.—Muriate of Yttria.

This compound has a striking resemblance to nitrate of yttria. Like that salt it dries with difficulty, and attracts moisture from the air. It does not crystallize, when evaporated, but forms a jelly.

#### SECTION IX.

## Chlorates or Hyper-oxy-muriates.

ART. 1.—Chlorate or Hyper-oxy-muriate of Potash.

The properties of this salt were discovered by Berthollet. It may be formed either by the direct mixture of liquid chloric acid with solution of potash or carbonate of potash;—or by passing chlorine gas, as it proceeds from the mixture of muriate of soda, sulphuric acid, and manganese (see Sect. II, Process 2), through a solution of caustic potash. This may be done by means of Woulfe's apparatus, using only one three-necked bottle in addition to the balloon. The tube which is immersed in the alkaline solution, should be at least half an inch in diameter, to prevent its being choked up by any crystals that may form. The solution, when saturated with the gas, may be gently evaporated, and the first products only of crystals are to be reserved for use; for the subsequent products consist of common muriate of potash only.

The chemical changes that occur in the production of chlorate of potash may be explained either on the old or the new theory. Let us (on the old hypothesis) suppose the oxy-muriatic acid, when first presented to the alkaline solution, to be divided into two portions; one of these gives up its excess of oxygen to the other half, and returns to the state of common muriatic acid, which combining with the alkali, forms muriate of potash.—The other portion, therefore, is oxy-muriatic acid, plus a certain quantity of oxygen; and this, uniting with another portion of alkali, forms a salt, which Mr. Chenevix has termed hyper-oxy-muriate. Strictly speaking, therefore, simply oxygenized muriate of potash does not exist; for the acid in this salt contains 65 per cent. of oxygen; whereas the oxy-muriatic acid must contain, if any oxygen be present in it, only 22.65 per cent.

It would be equally consistent with the theory of chlorine, either to suppose that the oxy-muriatic acid decomposes the water of the alkaline solution, forming, with its hydrogen, common muriatic acid, while another portion of chlorine unites with the oxygen thus set at liberty;—or that the change consists in the decomposition of potash, the oxygen of part of which is transferred to another portion of alkali, while the oxy-muriatic acid is partly expended in decomposing a triple compound of chlorine, oxygen, and partly in composing a triple compound of chlorine, oxygen, and per-oxide of potassium. In this view, hyper-oxy-muriate of potash is constituted of 1 atom of potassium weighing 40.5, 1 atom of oxy-muriatic acid = 33.5, and 6 atoms of oxygen = 45; or 100 parts consist of

Chlotine - - - - - - 28.
Potassium - - - - - - 34.
Oxygen - - - - - - 38.

On the theory of Mr. Dalton, one atom of oxy-muriatic acid weighing 29, deprives five surrounding atoms of the same acid of their oxygen, and constitutes one atom of hyper-oxy-muriatic acid = 54, which unites with an atom of potash = 42. These numbers are not very remote from those deducible from Mr. Chenevix's analysis, according to whom this salt is composed of

Hyper-	oxy	-m	uria	atic	ac	id	•	-	-	•	<b>58.3</b>
Potash	-	-	_	-	-	_	-	-	-	-	39.2
Water	-	•	-	-	-	-	-	-	-	-	2.5
•										-	
											100.

The water, however, is in too small proportion to be considered as

more than an accidental ingredient.

Even by the advocates of the simple nature of chlorine, two different views have been taken of this class of salts. By Gay Lussac, the chlorates are considered as compounds of chloric acid with alkaline and earthy bases; by Sir H. Davy, they are regarded as triple compounds of one atom of chlorine, one atom of metallic base, and six atoms of oxygen. But chloric acid being, as is deducible from the experiments of Gay Lussac, compounded of five atoms of oxygen with one atom of chlorine; there is no difference as to the facts, whatever there may be as to their explanation. This will appear from the following comparative statement.

According to D Hyper-oxy-muria chlorates consist o	tes or 🖁 1 atom	of metallic base of chlorine s of oxygen.
According to Gay Lussac, chlorates are composed of	1 atom of base, consisting of 1 atom of chlo- ric acid	1 atom metal 1 atom oxygen. 5 atoms oxygen 1 atom chlorine

It will easily be perceived, on examining these statements, that the same proportion of elements are assigned by both philosophers to the chlorates, and that the only difference is as to the manner in which those elements are arranged.

The chlorate of potash has the following qualities:

(a) It has the form of shining hexahedral laminæ, or rhomboidal plates.

(b) One part of the salt requires 17 of cold water for solution, but

five parts of hot water take up two of the salt.

(c) It is not decomposed by exposure to the direct rays of the sun,

either in a crystallized or dissolved state.

(d) When chlorate of potash is submitted to distillation in a coated glass retort, it first fuses, and, on a farther increase of temperature, yields oxygen gas of great purity. A hundred grains of the salt afford 75 cubic inches of gas (= about 25½ grains of gas), containing not more than three per cent. of nitrogen gas. Berzelius,

from the same quantity, obtained a much larger product of gas, viz. 39.15 grains = 112 or 114 cubic inches\*. And Gay Lussac found that 100 grains give 38.88 grains of oxygen, and 61.12 of muriate of potash, containing, he supposes, 28.93 chlorine and 32.19 potassium. The residue of this distillation (consisting, according to the new theory, of chlorine and potassium) Vauquelin asserts is sensibly alkaline; from whence it should appear that the capacity of saturation is less in chlorine than in chloric acid.

(e) The chlorate of potash has no power of discharging vegetable colours; but the addition of a little sulphuric acid, by setting chlo-

rine at liberty, developes this property.

(f) The salt is decomposed by the stronger acids, as the sulphuric and nitric acids. This may be proved by dropping a few grains of the salt into a little concentrated sulphuric acid. A strong smell will arise, and, if the quantities be sufficiently large, an explosion The experiments should, therefore, be attempted with will ensue. great caution. When this mixture is made at the bottom of a deep vessel, the vessel is filled with euchlorine gas, which inflames sulphuric ether, alcohol, or oil of turpentine, when poured into it; and also camphor, resin, tallow, elastic gum, &c. (Davy.)—By the action of sulphuric acid, regulated as already described, peculiar gaseous compounds result.

Muriatic acid, as has already been stated, disengages chlorine, and the addition of a few grains of the salt to an ounce measure of the acid, imparts to it the property of discharging vegetable colours.

(g) Chlorate of potash exerts powerful effects on inflammable

1. Rub two grains into powder in a mortar, and add one grain of sulphur. Mix them very accurately, by gentle triture, and then, having collected the mixture to one part of the mortar, press the pestle down upon it suddenly, and forcibly. A loud detonation will ensue.—Or, if the mixed ingredients be wrapped in some strong paper, and then struck with a hammer, a still louder report will be prodúced.

2. Mix five grains of the salt with half the quantity of powdered charcoal in a similar manner. On triturating the mixture strongly, it will inflame, especially with the addition of a grain or two of sul-

phur, but not with much noise.

3. Mix a small quantity of sugar with half its weight of the salt, and on the mixture pour a little strong sulphuric acidt. A sudden and vehement inflammation will be produced. This experiment, as well as the following, requires caution.

4. To one grain of the powdered salt, in a mortar, add about half a grain of phosphorus. The phosphorus will detonate, on the gentlest triture, with a very loud report. The hand should be covered

† Ann. de Chim. xcv, 101. \* Ann. de Chim. et Phys. v. 175.

<sup>\*</sup> A mixture of this kind is the basis of the matches, now generally used for the purpose of procuring instantaneous light. The bottle, into which they are dipped, contains concentrated sulphuric acid, which is prevented from escaping by a quantity of finely spun glass or the fibres of amianthus.

with a glove in making this experiment, and care should be taken that the phosphorus, in an inflamed state, does not fly into the eyes.—Phosphorus may also be inflamed under the surface of water by means of this salt. Put into a wine glass, one part of phosphorus with two of the salt; fill it nearly with water, and pour in, by means of a glass tube, reaching to the bottom, three or four parts of sulphuric acid. The phosphorus takes fire, and burns vividly under the water. This experiment requires caution, lest the inflamed phosphorus should be thrown into the eyes. (Davy.) Oil may also be thus inflamed on the surface of water, the experiment being made with the omission of the phosphorus, and the substitution of a little olive or linseed oil.

5. Hyper-exy-muriate of potash may be substituted for nitre in the preparation of gun-powder, but the mixture of the ingredients requires extreme circumspection. It may be proper also to state, that this salt should not be kept mixed with sulphur in considerable quantity, such mixtures having been known to detonate spontaneously.

## ART. 2.—Chlorate of Soda.

This salt may be obtained, by following the process already described, with the substitution of pure soda for potash; or by adding chloric acid to carbonate of soda, till the effervescence ceases. It is exceedingly difficult, however, to obtain it pure, by the first process, because it nearly agrees in solubility, with the common muriate of soda; and the second method is therefore preferable. It is soluble in three parts of cold water, and in rather less of hot, and is slightly deliquescent. It is soluble also in alcohol; but so also, according to Mr. Chenevix, is the common muriate. It crystallizes in cubes, or in rhomboids approaching the cube in form. In the mouth it produces a sensation of cold, and a taste scarcely to be discriminated from that of muriate of soda. In other properties it agrees with the similar salt with base of potash.

# ART. 3.—Chlorate of Ammonia.

This salt cannot be procured by the direct union of chlorine with pure ammonia, because these two bodies mutually decompose each other; as will appear from the following experiments:

1. Fill a pint receiver with chlorine gas; and pour into it half a drachm of the strongest solution of ammonia that can be procured.

A detonation will presently ensue.

2. Fill a four-ounce bottle with chlorine gas, and invert it in a cup containing four ounce-measures of the solution of pure ammonia. Presently the liquor will be absorbed, and a detonation will ensue,

which will throw down the bottle, unless firmly held by the hand.

In the bottle there remains a portion of nitrogen gas.

Though not capable, however, of being formed by the direct action of chlorine on solution of ammonia, yet an hyper-oxy-muriate or chlorate of ammonia, may be obtained by adding liquid chloric acid to solution of carbonate of ammonia, till the effervescence ceases. The solution must be evaporated by a very gentle heat, on account of the volatility of the salt; and it is best to allow it to evaporate

spontaneously at the temperature of the atmosphere.

The salt, thus obtained, has the shape of very fine needles. taste is extremely pungent. When heated, it detonates per se, like nitrate of ammonia, but at a lower temperature, and with a red When decomposed by heat in close vessels, a large quantity of chlorine is obtained, with a very small proportion of oxygen and nitrogen, and also of hydrogen and muriate of ammonia. Hence it appears that the hydrogen of the volatile alkali is more disposed to unite with the oxygen than with the chlorine contained in the chloric acid.

## ART. 4.—Chlorates with Earthy Bases.

1. Chlorate of Barytes.—To prepare this salt, chlorine gas must be received into a warm solution of barytes in water, till the barytes is saturated. The solution is to be filtered, and boiled with phosphate of silver, which decomposes the common muriate of barytes, and at the same time composes two insoluble salts, phosphate of barytes, and muriate of silver. Vauquelin finds the addition of acetic acid recommended by Chenevix, objectionable, and that the compounds of chloric acid are liable, if acetic acid has been employed, to detonate violently when heated. To judge when enough of the phosphate of silver has been used, add to a portion of the filtered liquor, a few drops of nitrate of silver, which, in that case, ought not to disturb its transparency. If too much phosphate of silver has been used, a drop or two of muriatic acid will discover it, and, in that case, the cautious addition must be made of some of the original solution, set apart for the purpose, to which no phosphate of silver has been added. It is from solution of chlorate of barytes, thus carefully prepared, that chloric acid is obtained by the intervention of sulphuric acid.

Chlorate of barytes has the form of four-sided prisms; its taste is pungent and austere; it requires for solution about four times its weight of water, at 50° Fahrenheit; and its solution, when pure, is not precipitated either by nitrate of silver or muriatic acid. By a red heat, it loses 39 per cent., and the residue is alkaline. From 2 calculation, founded on its decomposition by sulphuric acid, it ap-

pears to consist of

Barytes - - - - 46 Chloric acid - - - - 54

2. Chlorate of Strontites may be obtained by the direct action of chloric acid on carbonate of strontites. It is a deliquescent salt, having an astringent taste, and communicating to the flame of alco-

hol a fine purple tint.

3. Chlorate of Lime.—To the account of this salt, I think it proper to premise, that considerable uncertainty appears to me still to exist respecting its composition. It is even doubtful whether the substance, formed by exposing dry hydrate of lime to chlorine gas, is any thing more than a compound of that hydrate with chlorine.

This compound derives importance from its application to the art of bleaching; for its solution in water, even when there is no excess of chlorine, possesses bleaching properties; and produces whiteness in the unbleached part of goods, without destroying any delicate colours which they may contain. The dry compound, formed from hydrate of lime and chlorine gas, is extremely deliquescent; liquefies at a low heat; and is soluble in alcohol. It produces much cold by solution, and a sharp taste in the mouth. Its composition and properties have been investigated by Mr. Dalton, in two memoirs published in the 1st and 2d volumes of Dr. Thomson's Annals. He finds that the dry salt is a compound of two atoms of lime, one of acid, and six of water. By solution, one half of the lime is deposited, and a compound of one atom of lime and one of acid is dissolved by the water. The dry salt is much impaired by being long kept. It contains per cent. according to Dalton,

Chlorin	e	-	-	-	-	-	-	23.2
Lime	-	<b>-</b> .	-	-	-	-	-	38 <b>.4</b>
Water	7	-	-	-	-	-	-	38.4

100.

For an account of the remaining salts formed with chloric acid, Mr. Chenevix's paper in the Philosophical Transactions for 1802, and Vauquelin's memoir in the 95th volume of Annales de Chimie, may be consulted.

# SECTION X.

### Nitro-Muriatic Acid.

This acid may be formed most commodiously by mixing two parts by weight of colourless nitric acid with one of liquid muriatic acid. Proust employs only one of nitric to four of muriatic acid. Though the acids are both perfectly pale, yet the mixture becomes of a deep

red colour, a brisk effervescence takes place, and pungent vapours of

chlorine are evolved.

Considerable light has been thrown on the nature of this acid by the experiments of Sir H. Davy\*, who has rendered it probable that its peculiar properties are owing to a mutual decomposition of the nitric and muriatic acids, the oxygen of the former uniting with the hydrogen of the latter, in consequence of which water, chlorine, and nitrous acid, are the results. For every 101 parts in weight of real nitric acid (equivalent to 118 of hydro-nitric acid) which are decomposed, 67 parts of chlorine, he calculates, are produced. According to this view, it is not correct to say that aqua regia oxidates gold or platinum, since it merely causes their combination with chlorine. By long continued and gentle heat, nitro-muriatic acid may be entirely deprived of chlorine, and it then loses its power of acting on gold and platinum.

The nitro-muriatic acid does not form, with alkaline or other bases, a distinct genus of salts, entitled to the name of nitro-muriates; for, when combined with an alkali, or an earth, the solution yields, on evaporation, a mixture of a muriate and a nitrate; and metallic bodies dissolved in it yield muriates only. The most remarkable property of nitro-muriatic acid (that of dissolving gold, from whence it has been called aqua regia) will be described in the chapter on

that metal.

### SECTION XI.

# Murio-Sulphuric Acid.

MURIATIC acid gas is absorbed in considerable quantity by sulphuric acid. The compound has a brown colour, and when exposed to the air emits copious white fumes. It has no particular use.

By the action of a mixture of fuming muriatic acid on sulphuret of carbon, Berzelius obtained a solid white crystalline body, resembling camphor, and possessing some remarkable properties. Its analysis afforded

,				100.
Sulphurous acid Carbonic acid (and loss)	-	-	-	21.63
Muriatic acid				

It appears, therefore to consist of two atoms of muriatic acid, one of sulphurous acid, and one of carbonic acid.

\* Journal of Science, &c. i. 67.

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# APPENDIX.

## DESCRIPTION OF THE PLATES.

#### PLATE I.

FIG. 1. (a) A plain retort, the neck of which is shown introduced a proper length into the mouth of a plain receiver b. The dotted lines at c show the receiver with the addition of a tubulure, into which either a stopper, or bent glass tube, may be occasionally fixed.

Fig. 2. A glass alembic; a the body, and b the head, which are ground so as to fit accurately, and may be separated when necessary. The head b is so shaped, that any liquid, which may be condensed, collects into a channel, and is carried by the pipe c into the receiver.

Fig. 3. A separator, for separating liquids of different specific gravities. It is furnished with a ground stopper at a, and a glass stop-cock at b. The vessel is filled with the liquids that are to be separated (oil and water for example), which are allowed to stand till the lighter has completely risen to the top. The stopper a is then removed, and the cock b opened, through which the heavier liquid descends; the cock being shut, as soon as the lighter one is about to flow out.

Fig. 4. A glass vessel, termed a mattrass, useful for effecting the solution of bodies, which require heat before they can be dissolved, or long continued digestion, see vol. i. p. 31. The upper extremity of the long neck generally remains cool, and allows the vessel and its contents to be shaken occasionally.

Fig. 5. A glass bottle with a very thin bottom, and a projecting ring round the neck for suspending it over a lamp. These are use-

ful for effecting solutions on a small scale.

Fig. 6. An apparatus contrived by Mr. Pepys, for ascertaining the quantity of carbonic acid discharged from any substance by the addition of an acid. It consists of a bottle closed by a ground stopper. This stopper is perforated, and forms the lower part of a tube, which is twisted into the shape of a still-worm. In this worm, any water that escapes along with the gas, is condensed, and falls down again into the bottle. The experiment is made precisely as descri-

bed, vol. i. p. 241; and the loss of weight is determined at the close of the effervescence.

Fig. 7. Mr. Leslie's differential thermometer described, vol.

i. p. 80.

Fig. 8. (a) An air thermometer, for ascertaining the temperature of liquids. It consists of a bottle, partly filled with any coloured liquid, and partly with air, a glass tube of small bore, open at both ends, being either cemented or hermetically sealed into the bottle, so that its lower extremity may nearly touch the bottom of the bottle. The expansion of the included air, on the application of heat, drives the coloured liquid up the tube, and to an extent which may be measured by the application of a scale. The fig. b is another variety of the same instrument, described vol. i. p. 80.

Fig. 9. The original air thermometer of Sanctorio; see vol. i,

p. 80.

Fig. 10. A bent funnel for introducing liquids into retorts, with-

out soiling their necks.

Fig. 11. An adopter. The wider end admits the neck of a retort; and the narrower is passed into the mouth of a receiver.

Fig. 12. A section of an evaporating dish of Wedgwood's ware. Under this figure is a representation, without any number attached to it, of a small prong with a wooden handle, for holding an evaporating glass over a lamp.

Fig. 13. (a) A tubulated retort luted to (b) a quilled receiven the pipe of which enters the neck of a bottle (c) supported by a block

of wood.

Fig. 14. Different forms of jars for precipitations, with lips conve-

niently decanting the fluid from the precipitate.

Fig. 15. A tube blown in the middle into a ball, for dropping liquids. The ball is filled by the action of the mouth applied to the upper orifice, while the lower one is immersed in the liquid. To the former the finger is then applied; and, on cautiously removing

it, the liquid is expelled in drops.

Fig. 16. A bottle for ascertaining the specific gravity of liquids. When filled up to a mark in the neck, with distilled water of a given temperature, it should hold 1000, 2000, or any even number of grains. The quantity, which it is found to contain, of any other liquid of the same temperature, shows the specific gravity of the latter. For example, if it hold 1000 grains of water, and 1850 of sulphuric acid, the specific gravity of the latter is to that of water as 1850 to 1000.

#### PLATE II.

Fig. 17. An apparatus for procuring gases, without the possibility of their escaping into the room during the process, a circumstance which is of considerable importance, when the gas has an unpleasant smell or deleterious properties. Suppose that sulphureted hydrogen gas is to be obtained from sulphuret of iron and diluted sulphuric acid. The sulphuret of iron, in coarse powder, is put into the body of the gas bottle c, with a proper quantity of water. The acid

holder a is filled with diluted acid, the cock b being shut, and is then fixed into the tubulure of the gas bottle, to which it is accurately adapted by grinding. The bent tube d being made to terminate under a receiver filled with, and inverted in water, the perforated cock b is gradually opened, in consequence of which the acid descends into the gas bottle; and acts on the sulphuret of iron. If it be found necessary to renew the acid, without disturbing the apparatus, this may be done as follows. The cock b being shut, the stopper, which closes the acid holder, may be removed, and fresh acid be poured in, through the aperture. This may be repeated as often as is found necessary. The acid holder may be advantageously adapted, also, to a retort for certain distillations, such as that of muriatic acid.

Fig. 18. A plain gas bottle with sigmoid tube, the end, which is received into the bottle, having a ground stopper accurately fitted to the neck. For ordinary purposes (such as obtaining hydrogen gas from diluted sulphuric acid and iron filings) this apparatus answers perfectly well, and is much less costly. It is frequently made with a tubulure and glass stopper, and is then called a tubulated gas bottle.

Fig. 19. A gas funnel, useful in transferring any gas, from a wide-mouthed vessel into a jar of narrower diameter, or into a bottle. When employed for this purpose, it is held inverted, as shown by the figure, the pipe being admitted into the aperture of the bottle or jar, which is filled with and inverted in water, and the gas being made to pass into it in bubbles.

Fig. 20. Dr. Hope's Eudiometer. The manner of using it has al-

ready been described, vol. 1. p. 135.

Fig. 21. A modification of Dr. Hope's Eudiometer described, vol.

i. p. 136.

Fig. 22. A gas receiver, into the neck of which is cemented a brass cap, with a female screw for receiving a stop-cock. The vessel b is a glass flask, which may be made to communicate with the interior of the jar a, by opening the cock. When the apparatus is used, it is necessary to employ two stop-cocks, and not one only, as represented by the figure. Supposing that the weight of any gas is to be ascertained, the flask b is exhausted, by screwing it on the transfer of an air-pump; and, if great accuracy be required, it is proper to enclose a gage in the vessel. Let the flask be weighed when exhausted; then screw it upon the top of the receiver, containing the gas which is to be weighed; and open the communication, observing, by using a graduated jar, how much gas has been admitted. Suppose this to be 50 cubic inches. By weighing the flask again when full, we determine the weight of 50 cubic inches of the gas under examination. The experiment should be made when the temperature of the room is 60°, and when the barometer stands at 29.8.

Fig. 23. A plain jar for receiving gases, with a ground stopper. Fig. 24. An eudiometer for trying the purity of a mixture of gases containing oxygen gas, by means of nitrous gas. The process has already been described, vol. i. p. 309. The instrument should be accompanied with a phial, holding, when completely full, precisely a cubic inch.

Fig. 25. A wire stand, with a leaden foot, for the purpose of raising, above the surface of water within a jar, any substance which is to be exposed to the action of gas.

Fig. 25. (a) A bottle and tube for directing a small stream or a

few drops of water on any object.

Fig. 25. (b) A bottle with an elongated stopper, by means of which a single drop of any liquid can be taken up, and allowed to fall into any fluid under examination.

Fig. 26. An apparatus for showing that caloric exists in gases in a latent form. The application of it has been already described,

vol. i. p. 118.

Fig. 27. An apparatus for drying precipitates by steam, described, vol. i. p. 11.

Fig. 28. A graduated tube for ascertaining the strength of acids

and alkalies, see vol. ii. part ii.

Fig. 29, a and b. Tubes for exploding mixtures of hydrogen and other inflammable gases with oxygen gas, commonly termed the Eudiometer of Volta; see vol. i. p. 139.

## PLATE III.

Fig. 30. The common form of a Woulfe's apparatus. In this figure the retort a is represented plain, but it is better to employ a tubulated one. The use of this apparatus has already been described, vol. i. p. 31.

Fig. 31. A modification of the apparatus, which has been already described. In this figure, the mercurial trough is shown with a jar standing inverted in it, for the purpose of receiving any gas that may escape condensation by water.

Fig. 32. Mr. Pepys's improvement of Woulfe's apparatus descri-

bed, vol. i. p. 31.

### PLATE IV.

Figs. 33 and 34. Cuthbertson's apparatus, for exhibiting the composition of water, with the substitution of gazometers for the receivers originally employed by him. The apparatus has been described, vol. i. p. 146. Fig. 33 is an enlarged view of the conical brass piece, which is cemented into the bottom of the receiver, and through which the gases are conveyed.

Fig. 35. A gazometer of the most simple and common construc-

tion; see vol. i. p. 114.

Fig. 36. A gas holder, described, vol. i. p. 113.

Fig. 37. A galvanic trough; see vol. i. p. 160. The tube b shows the arrangement for decomposing water. The upper wire may be hermetically sealed into the tube, and the lower one passed through a cork, which should have a small slit cut in it, to allow the water to escape in drops as the gas is produced.

Fig. 38. The manner in which a candle may be burned in oxygen gas; see vol. i. p. 125.

Fig. 39. The combustion of iron wire in oxygen gas.

Fig. 40. Apparatus for decomposing water over red-hot iron or

charcoal; see vol. i. p. 149, 150.

Fig. 41. An apparatus for showing the diminution effected in the volume of hydrogen and oxygen gases by their slow combustion;

see vol. i. p. 141.

Fig. 42. A very simple and cheap contrivance for freezing quicksilver by muriate of lime and snow. The outer vessel of wood may be twelve and a half inches square, and seven inches deep. It should have a wooden cover, rabbeted in, and furnished with a handle. Within this is placed a tin vessel b b, standing on feet which are one and a half inch high, and having a projection at the top, half an inch broad, and an inch deep, on which rests a shallow tin pan c c. Within the second vessel is a third d, made of untinned iron, and supported by feet two inches high. This vessel is four inches square, and is intended to contain the mercury. When the apparatus is used, a mixture of muriate of lime and snow is put into the outer vessel a a, so as completely to surround the middle vessel b b. Into the latter, the vessel d, containing the quicksilver to be frozen, previously cooled down by a freezing mixture, is put; and this is immediately surrounded by a mixture of snow and muriate of lime, previously cooled to 0° Fahrenheit, by an artificial mixture of snow and common salt. The pan c c is also filled with these materials, and the wooden cover is then put into its place. The vessels are now left till the quicksilver is frozen. A more elegant, but more expensive apparatus, by Mr. Pepys, intended for the same purpose, is figured in an early volume of the Philosophical Magazine.

Fig. 43. A wire stand, consisting of an interior circle, and three straight pieces of wire proceeding from it in the same plane. Its

use is noticed, vol. i. p. 126.

Fig. 44. Sir H. Davy's apparatus for the analysis of soils described in his paper, which is copied into the third part of this work.

### PLATE V.

Fig. 45. Pictet's arrangement of an apparatus for showing the radiation of caloric, unaccompanied by light; see vol. i. p. 86.

Fig. 46. An oval copper boiler, for exhibiting the most important facts respecting latent caloric. The size of its different parts (except the width, which is 4 inches) may be learned from the scale affixed to the plate, which is abundantly sufficient to enable any intelligent workman to construct the apparatus. The collar joint and stuffing box, however, it is indispensably necessary to describe, especially as the former article of apparatus is generally constructed on a bad plan.

Fig. 47 is a section upon a larger scale, of the collar joint at b (fig. 46), made for the convenience of screwing together long or crooked metal tubes, without turning them round: a is a section of

the end of one of the tubes, and b that of the other which is to be attached to it; c is a collar which turns loose upon the shoulder of a, and screws upon b. By screwing this collar upon b, the end e e of the tube a is brought to press upon the part d of the tube b, without turning round either of those tubes. If upon d be laid a ring of linen cloth soaked in boiled linseed oil, the joint, when screwed up (if tolerably well made), will be impervious to steam as well as to water or air. The projection at d is for preserving the ring of cloth from being displaced, and for guiding the ends of both tubes, so as

to meet properly.

Fig. 48 is a section of a socket, for fixing the stem of a thermometer into a boiler or a digester, where there is much heat and pressure; b is a socket fixed on the outside of the boiler or digester, having a hole through it large enough to admit the bulb of the thermometer; a is a plug which screws into b, having a hole through its centre large enough to admit only the stem of the thermometer; cc is a loose round plate, concave on the upper side, having a hole through its centre just sufficient also to admit the stem of the thermometer. When the instrument is to be inserted, the plug a, and the plate c, must both be taken out of the socket. The bulb is then passed through it. The plate c is next slipped over the stem, and dropped into its place. Some flax, soaked in linseed oil, must next be wrapped round the stem, so as nearly to fill the socket. The plug a must then be screwed in, till the flax be compressed so as to make the whole sufficiently tight. The opposite surfaces of the plate c, and the plug a are made concave, for the purpose of compressing the flax round the stem of the thermometer.

### PLATE VI.

Figs. 49, 50, 51. Sections of crucibles.

Fig. 52. A muffle; see vol. i. p. 29.

Fig. 53. Stands for raising the crucible above the bars of the grate; a one adapted to Mr. Aikin's blast furnace; b one of the common form.

Fig. 54. A skittle-shaped crucible.

Fig. 55. Mr. Aikin's portable blast furnace. It is composed of three parts, all made out of the common thin black-lead melting pots, sold in London for the use of the gold-smiths. The lower piece c is the bottom of one of these pots, cut off so low as only to leave a cavity of about an inch, and ground smooth above and below. The outside diameter over the top is five and a half inches. The middle piece, or fire-place a, is a larger portion of a similar pot, with a cavity of about six inches deep, and measuring seven and a half inches over the top, outside diameter, and perforated with six blast holes at the bottom. These two pots are all that are essentially necessary to the furnace for most operations; but when it is wished to heap up fuel above the top of a crucible contained within, and especially to protect the eyes from the intolerable glare of the fire when in full heat, an upper pot b is added, of the same dimensions

as the middle one, and with a large opening in the side, cut to allow the exit of the smoke and flame. It has also an iron stem, with a wooden handle (an old chisel answers the purpose very well) for re-

moving it occasionally.

The bellows, which are double (d), are firmly fixed by a little contrivance which will take off and on, to a heavy stool, as represented in the plate; and their handle should be lengthened so as to make them work easier to the hand. To increase their force on particular occasions, a plate of lead may be firmly tied on the wood of the upper flap. The nozzle is received into a hole in the pot c, which conducts the blast into its cavity. From hence the air passes into the fireplace a, through six holes of the size of a large gimlet, drilled at equal distances through the bottom of the pot; and all converging in an inward direction, so that if prolonged, they would meet about the centre of the upper part of the fire. Fig. 56 shows the distribution of these holes in the bottom. The large central hole is intended to receive the stand a, fig. 53, which serves for supporting the crucible.

No luting is necessary in using this furnace, so that it may be set up and taken down immediately. Coke or common cinders, taken from the fire when the coal just ceases to blaze, sifted from the dust, and broken into very small pieces, forms the best fuel for higher heats. The fire may be kindled at first by a few lighted cinders, and

a small quantity of wood-charcoal.

The heat which this little furnace will afford is so intense, that its power was, at first, discovered accidentally by the fusion of a thick piece of cast iron. The utmost heat procured by it was 167° of Wedgwood's pyrometer piece, which was withdrawn from a Hessian crucible, when actually sinking down in a state of porcellanous fusion. A steady heat of 155° or 160° may be depended on if the fire be properly managed, and the bellows worked with vigour\*.

By a letter from Mr. Aikin, I have learned, also, a convenient way of exhibiting, in a lecture, and performing at other times, the process of cupellation, by means of this furnace. It consists in causing a portion of the blast to be diverted from the fuel, and to pass through a crucible in which the cupel is placed. This arrangement supplies air; and the whole may be seen by a sloping tube run through the cover of the crucible. Fig. 57 shows the furnace, when used for this purpose; a a the furnace; b the perforated stopper for the central blast; c c a portion of earthen tube, through which the air passes, and is heated during this transit; e a piece of soft brick perforated to admit the earthen tube f, which may be kept open for inspecting the process. No luting is required, except to join f to e.

Fig. 58. Knight's portable furnacet, composed of strong iron plate lined with fire lute, the inside diameter six inches: a shows the grate; b the ash pit door; d the door of the fire-place when used

<sup>\*</sup> See Philosophical Magazine, vol. xvii. p. 166. † This furnace is also described in vol. i. p. 2, 3.

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as a sand heat; ee two holes opposite to each other for transmitting a tube; g an opening for a retort neck, when used for distilling with the naked fire.

 $F_{1G}$ . 59. A different view of the same furnace; a the grate; c the register to the ash pit; f a small door, with a contrivance for supporting a muffle. The other letters correspond with the expla-

nation of the preceding figure.

For this furnace the proper fuel when it is used as a wind furnace, is wood-charcoal, either alone, or with the admixture of a small proportion of coke. For distillation with a sand heat, charcoal, with a little pit coal, may be employed.

#### PLATE VII.

Fig. 60 represents a fixed furnace, which I find very useful, because it may either be employed as a wind furnace or for distillation with a sand heat. Its total height outside is thirty-three inches, and the outside square is eighteen inches, or two bricks laid lengthwise. The thickness of the sides of the furnace is the breadth of a brick, or four and a half inches; but whenever there is room, it is better to make them nine inches in thickness. From the top of the furnace to the grate, which is moveable, and supported by two bearers, the height is thirteen inches; and at c is a double Rumford door; or in preference, a hole closed by a moveable earthen stopper, for introducing fuel. The ash pit should have a register door. The chimney is four inches wide by three high, and may either be furnished with a damper or not. On the top of the furnace a cast-iron ring is fixed, ten inches inside diameter, three inches broad, and half an inch thick. It is secured in its place by three iron pins, passing through three equidistant holes in the ring, and bent at the distance of nine inches at a right angle. These serve the purpose of binding the ring firmly into the brick-work. The sand pots are of different sizes; and a variety of them may be made to fit the same ring, by varying the breadth of their rims, as shown fig. 71. The brick should be cemented together, at least for the inner half of their breadth, by loam, or by a mixture of Stourbridge clay, with two or three parts sand, and a proper quantity of water.

When this is used as a wind furnace, the opening in the side is to be closed by its stopper; or, if a Rumford door be employed, it must be defended from the fuel by a fire tile. The fuel (coke) is introduced at the top, which is occasionally covered by a fire tile. When distillation with a sand heat is performed, the sand pot rests on the iron ring, and the fuel, which may be common pit coal, is added through the opening in the side. It may be proper to state, that, in order to receive a sand pot of as large a size as possible, the upper course of bricks should be bevelled within the furnace; and the

width at the top may exceed a little that at the grate.

The best Stourbridge or Newcastle-on-Tyne fire-bricks are neces-

sary in constructing this and the following furnaces.

Fig. 61 is a longitudinal section of a wind furnace, invented by Mr. Knight, with an additional chamber for applying the waste heat

to useful purposes: a the internal cavity, which is square, for containing the fuel and the crucible: b the flue passing into a hot chamber c; an appendage particularly useful for drying luted crucibles, or bringing them to a proper temperature for the furnace; for roasting ores and various other purposes: d the flue connecting it with the vertical chimney e; which, to produce a strong heat, should never be less than thirty or forty feet high: ff covers, consisting of twelve-inch Welsh tiles, with handles: g the stoke hole, through which no more of the fire is seen than what appears between the grate and the bearing bar h. This space is left for the double purpose of raking the fire, and occasionally taking out the bars: k the ash pit, which is sunk below the level of the ground, and is covered, where it projects at l, by an iron grating.

The best situation for this furnace, is an angle of the laboratory, the chimney being in the corner, as represented in the sketch. By this arrangement, the operator is spared the disagreeable necessity of scorching his legs, by standing opposite the stoke hole, while the backs of his legs are exposed to a current of cold air rushing to the

furnace.

Figs. 62 and 63 are different views of a furnace invented by Mr.

Knight, and convertible to various purposes.

The inside of this furnace is nine inches square, and sixteen inches deep from the top to the grate. The face of the opening at g rises at an angle, which makes the back part five inches higher than the This contrivance enables us completely to cover a large retort with fuel, without obstructing the passage of the air, and also relieves partly the weight of the cover, when it requires to be moved. The walls of the furnace are at least a brick and a half thick, and as much more as local convenience will allow. By sinking the ash pit below the level of the ground, at i, the height of the furnace needs not exceed eighteen inches, which renders the management of the fuel much more easy, and subjects the face and hands less to the action of the heat. The ash pit a, must be at least eighteen inches deep, below the surface of the ground, and more if convenient. It must have an opening, projecting from it three or four feet, to be covered with boards, and with an iron grating next the furnace. This preserves the legs of the operator from the action of the fire.

The grate b is formed of separate bars, each of a triangular shape, three fourths of an inch apart, and resting on two bearers. In the front of the furnace, an iron bar is to be placed to support the brickwork, and to leave an opening, through which the bars may occasionally be drawn out, and the fire raked and cleared of the slag. The chimney e is two and a half inches from the top, and four and a

half wide by two and a half high.

To fit this furnace for occasional distillation with the naked fire, an opening, d, fig. 62, is left on one side, which is filled up, when not wanted, by five pieces of soft fire-brick, cut to a proper shape, and secured by a clay lute. It is proper, also, to be provided with other pieces, having arched openings for transmitting the neck of a retort. One of these pieces may have a round hole for occasionally trans-

mitting a tube, and a corresponding hole, h, fig. 63, must then be made in the opposite side of the furnace, to be closed, when not

wanted, with a stopper.

Figs. 64 and 65 represent a sand heat, for containing flat evaporating vessels; the depth from back to front two feet; the width, agreeably to the scale, six feet. At the front is a rim four inches deep, consisting of a piece of iron plate, which is fastened at each end into the wall. The floor or bottom, e e, is formed of cast-iron plates, which rest upon each other in corresponding rabbets. The advantage of several small plates, over one large one, is the cheapness and facility, with which they are replaced, if cracked by the heat, an accident of not unfrequent occurrence. The joints are secured by a fire lute, which effectually prevents the sand from falling through. The fire place is shown by b; at the bottom it has a grate ten inches long, by eight wide. The flame and smoke circulate first through the flue c, and then through the returning flue d, which conveys the smoke to the chimney g. In constructing the flue beneath the grate, a row of bricks, set edgeways, answers the purpose, and serves also to support the inner edge of the plates.

It is adviseable to cover the sand heat with a sloping roof, which may be formed of lath and plaster, and supported by side walls. The lowest part of the roof may be foremost, and about three feet above the edge of the iron plates. It is, also, necessary to have an air flue, nearly at the top of the back wall, under the dome or roof, to be closed occasionally by a door. This must open into the chimney, in which case it serves the purpose of carrying off noxious vapours.

#### PLATE VIII.

Figs. 66, 67, 68, are the section and plans of a reverberatory furnace for experimental purposes. In this furnace, the fuel is contained in an interior fire-place; and the substance, to be submitted to the action of heat, is placed on the floor of another chamber, situated between the front one and the chimney. The flame of the fuel passes into the second compartment; by the form of which it is concentrated upon the substance exposed to heat, which is not confined in a separate vessel or crucible, but placed on the floor of the furnace. When reduced to a state of fusion, the melted mass is allowed to flow out through a tap-hole at h. The dimensions of this furnace it is scarcely possible to state, as they vary so considerably in different parts of it; but they may be ascertained by referring to the figures, and by the application of the scale. In all three figures, a represents the ash pit; b the grate composed of moveable bars; c the door at which the fuel is introduced; d a door in the side of the chamber, for the purpose of inspecting the process; e the floor of the furnace which descends, and is gradually contracted towards the back part; f another door for introducing and stirring the materials; g the back part of the furnace, immediately under the chimney; h the taphole; i the chimney.

Figs. 69 and 70, exhibit a cupelling or enamelling furnace. The

form of this should be an oblong square; its dimensions being regulated by that of the muffle, which should go home, to the back, its front edge lodging on the mouth of the furnace. On each side of the muffle, two inches and a half must be left, to let the fuel pass readily underneath, where there should also be a similar space. A stoke hole must be left on the other side, but the situation of the view will not admit its being shown. Before the muffle, is a projecting ledge or shelf, shown at e, which is intended to support any thing that is to be put into the muffle. Two twelve-inch tiles, worked in along with the bricks, will answer this purpose. In both figures, a shows the ash pit; c the grate; d the muffle; e the opening for introducing the muffle; f the chimney, and g the cover.

Fig. 71. Sand pots with rims of different sizes.

Figs. 72, 73. Dr. Black's portable furnace, made of sheet iron lined with fire clay. Its dimensions, as they vary in almost every part, will best be learned from the scale; a the fire place; b the chimney; c the ash pit; d the door of the ash pit; e a register for regulating the quantity of air admitted to pass through the fuel.

Fig. 74. Mr. Chenevix's wind furnace. This is rudely sketched in Nicholson's Journal, from which the more accurate figure in plate viii. is taken. This furnace Mr. Chenevix describes as follows: "I have constructed a wind furnace, which, in some respects, is preferable to the usual form. The sides, instead of being perpendicular, are inverted; so that the hollow space is pyramidal. At the bottom the space is twelve inches square, and at the top only eight. The perpendicular height is seventeen inches, from the top to the grate. This form unites the following advantages. 1. A large surface is exposed to the air, which, having an easy entrance, rushes through the fuel with great rapidity. 2. The inclined sides act as reverberators. 3. The fuel falls of itself, and is always close to the grate."

In the figure, a represents the grate; c c are two bricks which can be let in at pleasure, to diminish the capacity: l is another grate which can be placed on the bricks c c, for occasional purposes: d d are bricks, which can be placed on the grate b, to diminish the capacity of this part of the furnace; e the cover. Both set of bricks should

be ground to the slope of the furnace.

In the construction of every furnace, which is intended to produce a strong heat, lime or mortar should be avoided and the bricks should be set in loam, or Stourbridge clay, worked up with water and sand, inserting occasionally pieces of sheet iron, bent twice in opposite directions at right angles. The furnace should be allowed to remain some weeks, after setting up, before it is used; and before raising a strong heat, a gentle fire should be sometimes kindled in it, the strength of which may be gradually increased. When a strong blast is expected, it is necessary to bind the brick-work together, externally, by strong iron bars and plates, kept in their places by screws. The chimney should be nine inches wide, and raised to as great a height as circumstances will admit.

The coke of pit coal is the only fuel fitted for exciting an intense heat, and should be used in all cases, except in the reverberatory, and in distillations with the sand bath, when pit coal may be employed. The charcoal of wood is adapted principally to portable furnaces.

#### PLATE IX.

Fig. 75. The galvanic battery called couronne de tasses described vol. i. p. 161.

Fig. 76. Apparatus for obtaining the elements of water in sepa-

rate tubes; see vol. i. p. 166.

Fig. 77. The pile of Volta; see vol. i. p. 160.

Fig. 78. Section of a galvanic trough, to explain the theory of the

excitation of galvanic electricity; see vol. i. p. 174.

Fig. 79. Apparatus for obtaining oxygen and hydrogen gases. from separate quantities of water not in contact with each other; see vol. i. p. 167.

Fig. 80. Two agate cups connected by moistened amianthus;

see vol. i. p. 168.

Fig. 81. Two gold cones similarly connected, ibid.

Fig. 82. Agate cups similarly connected with an intermediate vessel i; see vol. i. p. 169.

Fig. 83. Apparatus for procuring potassium from potash and iron

filings described vol. i. p. 184.

Fig. 84. Apparatus for firing gases by electricity, or submitting

them to electrical discharges, vol. i. p. 115.

Fig. 85. Pepys's improved gas-holder; a a small iron retort placed in the fire with a jointed conducting tube b, which is admitted into the vessel at c. This is shown on a larger scale in a different part of the plate. The letter d is placed on the body of the reservoir, and near the central pipe, which descends from the cistern e to nearly the bottom of the vesiel. At f a glass tube is fixed, which shows the height of the water within the vessel. When a jar is intended to be filled with gas from the reservoir, it is placed, filled with water and inverted in the cistern e. The cocks 1 and 2 being opened, the water descends through the pipe attached to the latter, and the gas rises through the cock 1. By raising the cistern e to a greater elevation, any degree of pressure may be obtained; and a blow-pipe may be screwed on the cock at the left side of the vessel.

# ADDITIONAL PLATES.

### PLATE X.

Fig. 1. A view of Glauber's apparatus for distillation.

a. The ash-hole of the furnace.

bc. The door of the furnace.

d. An opening for a sand bath.

f. A pipe, going from the distilling vessel.

The first crooked pipe, fitted to the pipe

g. The first crooked pipe, fitted to the pipe f.

h. A receiver fitted to that pipe, and set in a tub of water, for accelerating the operations: which receiver hath a cover with two holes, through the first whereof goeth a single crooked pipe, and through the other two crooked pipes, whereof one goeth into the receiver, as did the single, and the other out of the receiver h, into hh; i the tub of water; m a third pipe. By this way flowers are sublimed, and spirits distilled speedily, and in great quantity.

Fig. 2. Mr. William Hembel, jr's. apparatus for distillation.

"A Woulfe's apparatus" (says this gentleman, in the note he has given in the American edition of the New Edinburgh Encyclopædia, vol. 5, p. 802) "with tubes of safety may answer very well for demonstrations at a public lecture: but, for processes in which considerable quantities of gas are evolved, and the saturation is to be effected under great pressure, they are totally inadequate. If the lower orifice of the tube is much immersed below the surface of the liquid, the accumulated gas will act similar to condensed air in the experiment of the hydrostatic fountain, and force the liquid out of the bottle until the orifice of the tube is exposed; then the gas will also escape; thus occasioning a double loss of products, and that whether straight or Welter's tubes be used.

"Plate CXLII. No. 2. fig. 4. represents our method of connecting any number of bottles, by which tubes of safety are superseded; yet the liquid can be saturated with gas, by as much pressure as the tenacity of the glass will resist: with the further advantage of being able to change the surface of the liquid at pleasure, without injury

to the product.

"The apertures of the tubes h, k, m, o, merely perforate their respective corks; whilst the tubes i, l, n, &c. descend very near the bottoms of the bottles. Into the bottle c, a small quantity of water is introduced, to engage the impure gas which may come over. The bottles e and g, contain the liquid to be saturated with the gas;—a similar arrangement of long and short tubes are to be used for any additional number of bottles.

"On introducing into the retort, the substance from which the gas is to be extricated, and adding an acid, an action will take place. The evolved gas will pass through the liquid in the bottles as usual.

When the gas ceases to be further evolved, a condensation will take place in the retort; then the liquid in the bottle c, e and g, will yield to the pressure of the incumbent atmosphere, (acting through the aperture of the tube o,) and pass into the bottles b, d and f. But as the apertures of the short tubes h, k and m, terminate with the lower surface of their respective corks, and the liquid in the bottles does not reach those apertures, the liquid can pass no further.

"It will then be only necessary to excite a fresh action by adding more acid in the retort, when the gas will accumulate in the receiver and empty part of bottle b. When the elastic force of the accumulated gas is sufficient to support a column of the liquid, equal to the height of one leg of the tube i, the liquid will rise and pass into the bottle c, the gas will follow and pass in the bottle d, and by pressing on the surface of the contained liquid will force it over into the bottle e, after which, the liquid in f will be forced in g, when the process of saturation will go on as before.

"There will be a great economy of acid, if the subsequent additions are not added until after an absorption has taken place, as the surface of the liquid will thereby be frequently changed, and the absorption of gas considerably accelerated.—For saturating water with muriatic and ammoniacal gas, or preparing hyper-oxy-muriate of potash on a large scale, demijohns may be substituted for the bottles d, e,

f, &c." Hembel, jun.

Fig. 3. Dr. Wollaston's cryophorus.

Fig. 4. Apparatus for impregnating water with oxy-muriatic acid gas.

Fig. 5. Apparatus for extricating phosphureted hydrogen gas.

a Is a block of wood, shaped as in the engraving; the inclined plane of which is hollowed out in the middle, to receive the neck of the retort; b b strings, or other contrivance for fastening down the retort, after the materials are introduced. The figure sufficiently explains the other intentions to be answered in the operation.

Fig. 6. A very convenient table furnace.

It is simply a large earthen pot, such as is in constant family use turned upside down. Before the pot is baked, an opening is cut in its side, as represented in the plate; another opening (circular) is made in the bottom (the top of the furnace), and several smaller ones near the bottom, for permitting the smoke, &c. to escape. Such a furnace can be readily procured for 25 or 30 cents of any potter; and is an excellent substitute for those of a more costly nature. It may be used for a great variety of purposes, requiring only a lamp heat. It will answer for the purposes of analysis; for distilling most of the acids, and indeed for almost every common occasion. Two or three of different heights, and with holes of various sizes at the bottom, will be found adapted for nearly every purpose.

<sup>\*</sup> It may not be improper here to remark, that the above description is rendered useless in the Encyclopædia, owing to the engraving of the apparatus being defective in the letters of reference—and it would be obviously judicious in the editors to cancel the present plate and replace it by one more perfect. C.

### PLATE XI.

Account of Dr. Wollaston's Scale of Chemical Equivalents, from Thomson's An. of Philos. vol. 4, p. 176.\*

This scale is of so much convenience to the practical chemist, that I seize the earliest opportunity to make it known to my readers in general. It gives the composition of any weight whatever of any of the salts contained on the scale, the quantity of any other salt necessary to decompose it, the quantity of new salt that will be formed, and many other similar things, which are perpetually occurring to the practical chemist, and cannot be answered without an arithmetical calculation. I have used such a scale for above six months, and found it attended with numberless advantages. I cannot undertake to explain the instrument, either more clearly, or in fewer words, than Dr. Wollaston himself has done in his own paper. I conceive, therefore, that the best thing I can do is to present my readers with the following extract from that paper, which contains the most material part of it, as far as the explanation of the instrument is concerned:—

"It is not my design, in the table which follows this paper, to attempt a complete enumeration of all those elements or compounds which I suppose to be well ascertained, but merely to include some of those which most frequently occur. I do not offer it as an attempt to correct the estimates that have been formed by others, but as a method in which their results may be advantageously applied in forming an easy approximation to any object of our

inquiries.

"The means by which this is effected may be in part understood by inspection of the Plate [II.], in which will be seen the list of substances intended to be estimated, arranged on one or the other side of a scale of numbers in the order of their relative weights, and at such distances from each other, according to their weights, that the series of numbers placed on a sliding scale can at pleasure be moved, so that any number expressing the weight of a compound may be brought to correspond with the place of that compound in the adjacent column. The arrangement is then such, that the weight of any ingredient in its composition, of any re-agent to be employed, or precipitate that might be obtained in its analysis, will be found opposite to the point at which its respective name is placed.

"In order to show more clearly the use of this scale, the Plate exhibits two different situations of the slider, in one of which oxy-

<sup>\*</sup> Dr. Wollaston's paper is published in the Philosophical Transactions for 1814, part i.

gen is 10, and the other bodies are in their due proportion to it, so that carbonic acid being 27.54, and lime 35.46, carbonate of lime is

placed at 63.

"In the second figure, the slider is represented drawn upwards till 100 corresponds to muriate of soda; and accordingly the scale then shows how much of each substance contained in the table is equivalent to 100 of common salt. It shows, with regard to the different views of the analysis of this salt, that it contains 46.6 dry muriatic acid, and 53.4 of soda, or 39.8 sodium, and 13.6 oxygen; or if viewed as chloride of sodium, that it contains 60.2 chlorine, and 39.8 sodium. With respect to re-agents, it may be seen that 283 nitrate of lead, containing 191 of litharge employed to separate the muriatic acid, would yield a precipitate of 237 muriate of lead, and that there would then remain in solution nearly 146 nitrate of soda. It may at the same time be seen, that the acid in this quantity of salt would serve to make 232 corrosive sublimate, containing 185.5 red oxide of mercury, or would make 91.5 muriate of ammonia, composed of 6 muriatic gas (or hydro-muriatic acid), and 29.5 ammonia. The scale shows also, that for the pupose of obtaining the whole of the acid in distillation the quantity of oil of vitriol required is nearly 84, and that the residuum of this distillation would be 122 dry sulphate of soda, from which might be obtained, by crystallization, 277 of Glauber salt, containing 155 water of crystallization. These and many more such answers appear at once by bare inspection, as soon as the weight of any substance intended for examination is made by motion of the slider correctly to correspond with its place in the adjacent column.

"With respect to the method of laying down the divisions of this scale, those who are accustomed to the use of other sliding-rules, and are practically acquainted with their properties, will recognise upon the slider itself the common Gunter's line of numbers (as it is termed), and will be satisfied that the results which it gives are the

same that would be obtained by arithmetical computation.

"Those who are acquainted with the doctrine of ratios, and with the use of logarithms as measures of ratios, will understand the principle on which this scale is founded, and will not need to be told that all the divisions are logometric, and consequently that the mechanical addition and subtraction of ratios here performed by juxta-position, correspond in effect to the multiplication and division of the numbers by which those ratios are expressed in common arithmetical notation.

"To others who are not equally conversant with the nature of logarithms, and consequently have not so correct a conception of the magnitude of ratios, some further explanation of the mode in which the scale of equivalents is constructed, will, I presume, be

acceptable.

"They will observe, that the series of natural numbers are not placed at equal intervals on the scale; but that at all equal intervals are found numbers which bear the same proportion to each other. In fig. 3, some of the larger intervals alone are represented

on a line similarly divided. The succession of intervals, marked A, B, C, D, E, are all equal, and at these points of division are placed numbers 1, 2, 4, 8, 16, which increase progressively by the same ratio. And since the series 3: 6: 12: 24 increase in the same ratio of 1 to 2, these intervals a, b, c, d, e, are the same as the former. At another succession of different yet equal intervals, marked F, G, H, I, are placed numbers 1, 3, 9, 27, which increase regularly by an equal ratio of 1 to 3; and by means of a pair of compasses it would be found that the interval from 2 to 6, or from 6 to 18 (which are the same ratio of 1 to 3), is exactly equal to F G, the interval between 1 and 3. As any single space represents any one ratio, so the sum of any two or three equal spaces represent a double or triple ratio. If 1 be increased three times by the ratio of 1 to 2, it becomes 8, which bears to 1 triple the ratio of 2 to 1. This ratio is therefore represented by A D, which is the triple of A B.

"The distances of the intermediate numbers 5, 7, 10, 11, 13, &c. from 1 are likewise made proportional to the ratios which they bear to 1, and are easily laid down by means of a table of logarithms; for as these are arithmetic measures of the ratios which all numbers bear to unity, the space proportionable to them become linear re-

presentations of the same quantities.

"As the entire spaces AD, AE, represent the ratios of 8 and of 16 respectively to 1, so the difference DE represents the ratio of 8 and 16, which stand at D and E, to each other. And in the same manner any other space, kl, represents correctly the ratio of 7 to 13; so that the measure of a fraction expressed by quantities that are incommensurate is rendered as obvious to sight as that of any simple multiple. And if a pair of compasses be opened to this interval, and transferred to any other part of the scale, the points of the compasses will be found to rest upon numbers bearing the same proportion to each other as those from which the interval was transferred.

"It is exactly in this manner that the various points in the column of equivalents indicate the several quantities sought in any given position of the slider. The relative distances, at which the articles are placed, represent so many different openings of the compasses rendered permanent and presented to view at once. In the table, which I shall place at the end of this communication, the relation of the various substances enumerated to each other is expressed by numbers.\* In the engraved scale of equivalents, the ratios of these numbers are represented by logometric intervals at which they are placed, their several positions being determined by those of their respective numbers on the slider, which is logometrically divided. Consequently all the several points in the column of equivalents will indicate numbers in the same due proportions to each other, whatever part of the scale may be presented to them. Those who seek information may obtain it by inspection; those who already

<sup>\*</sup> This has reference to the Philosophical Transactions. Dr. Thomson has not introduced the table in his Annals. C.

possess it may be able to correct the positions of some articles by direct comparison with the best analyses upon record, in whatever numbers the results of those analyses may happen to be expressed."

A Substitute for Woulfe's or Nooth's Apparatus, by ROBERT HARE, M. D. Professor of Chemistry in the Medical Department of the University of Pennsylvania, and Member of various Learned and Scientific Societies. With a plate.

Few subjects have more occupied the attention of chemists, than the means of impregnating fluids with gaseous substances. The contrivances of Woulfe and Nooth, especially the former, have been almost universally used; and have gained for the inventors merited celebrity. Various improvements in Woulfe's bottles have been devised. Still I believe an apparatus replete with similar advantages, but less unwieldy, less liable to fracture; and having fewer junctures to make at each operation, has been a great desideratum with every practical chemist. It has, however, ceased to be so with me, since I contrived the apparatus which I am about to describe.

Fig. 1. represents 3 jars placed concentrically within each other, and so proportioned and situated, as to admit two open-necked concentric bell glasses alternatively between them. The neck of the exterior bell glass is introduced into the tubulure of the receiver above, and receives the neck of the interior bell glass. Into this is inserted a trumpet-shaped tube. The two interior jars are furnished with feet F, f. In order to put this apparatus into operation, remove (without taking them apart) the bell glasses, receiver, and tube from the jars. Pour into the latter the fluid, to be impregnated, till it reaches the height marked by the dots. The funnel mouth, m, of the receiver being provided with a suitable cork soaked in wax, fasten into it firmly the beak of the retort, containing the generating materials. The bell glasses are then to be replaced in the jars, and arranged as in the figure. It must be self-evident that the gas proceeding from the retort, (if the juncture at m be air tight) must press on the fluid in the innermost jar, through the trumpet-shaped tube. If not imbibed with adequate speed, it must soon press on the fluid at a, causing it to subside to the narrow part of the foot f, and thus to expose a much larger surface. If the absorption be still inadequate, a further subsidence must ensue, and the gas escaping round the brim of the interior bell glass will act on the fluid at b, and enlarge its surface by depressing it to the narrow part of the foot F. Should the increased pressure and more extended contact thus obtained, be still incompetent to effect a complete absorption, the excess of the gas may escape round the brim of the external bell glass into the atmosphere.

But so effectual is this process in promoting impregnation, that I have obtained strong muriatic acid in the central jar, without producing any sensible acidity in the outside one. Absorption into the retort or receiver, is prevented by not allowing as much fluid to be above the mouth of the trumpet-shaped tube, as would be competent to fill the cavity between it, and the termination of the open neck of the exterior bell glass at t. As this neck rises about 2 or 3 inches into the receiver, it prevents any foul matter which may condense or boil over, from getting into the jars. If practicable, it would be better that the bell glasses, and tube, and receiver, should be united together while hot, at the glasshouse. If all could not be joined in this way, it would still be advantageous to unite thus the receiver, and the exterior bell glass. The interior bell and tube might then be fastened together, by grinding or luting. As yet I have only used lutings of waxed cloth, or cork. It may be proper to point out, that 3 or more concentric bell glasses, and 4 or more jars, might be used. The union of the bells, receiver, and tube once effected, it is hardly more troublesome to use 3 than 2. When the fluid in the central jar is saturated, this may be emptied and replenished from the middle jar, the latter from the external one. Then supplying the exterjar, the latter from the external one. nal jar anew, the process may be continued.

The other figures are to explain an apparatus on the same principle, constructed of hollow, oblong paralellopipeds, differing in length more than in breadth; so as to allow a serpentine tube to wind into the interior, and deliver gas under a vessel shaped like

B Ł.

Fig. 2. represents a vertical section of the whole as when situated for use.\*

Fig. 3. a vertical section of the lower vessels only.

Fig. 4. a vertical section of the covers alone.

Fig. 5. a horizontal section, or ground plan of the lower vessels. The upper vessels are so proportioned as to divide the distances

between the lower ones equally.

It may be well to mention, that this apparatus, from the facility with which it may be cleaned and inspected internally, admits of being made of porcelain or stone ware.† I have had a cylindrical one constructed of the latter material, in which the covers are in one piece, with a tube in the centre for introducing gas. The apparatus may be made more efficacious, by drilling a series of small holes round the brims of the bell glasses or covers, so as to cause the gas, instead of passing round the brims in large bubbles, to divide itself into very small ones. By this means it will be more thoroughly intermingled with fluid.

† The apparatus may also be made of glass bottles, duly proportioned, and cut (truncated) alternately near the shoulder and near the bottom.

<sup>\*</sup> Excepting, that the covers ought to be so depressed, as that their brims may be lower than the bottoms of the interior vessels over which they are placed respectively. This is necessary to prevent the gas from escaping, ere it have access to the surface of the fluid beneath those bottoms.

A New Theory of Galvanism, supported by some Experiments and Observations made by means of the Calorimotor, a new Galvanic Instrument. Read before the Academy of Natural Sciences, Philadelphia,\* by Robert Hare, M. D. Professor of Chemistry in the Medical Department of the University of Pennsylvania, and Member of several Learned Societies.

### [With an engraving.]

I have for some time been of opinion that the principle extricated by the voltaic pile is a compound of caloric and electricity, both being original and colateral products of galvanic action.

The grounds of this conviction and some recent experiments

confirming it, are stated in the following paper.

It is well known that heat is liberated by the voltaic apparatus, in a manner and degree which has not been imitated by means of mechanical electricity; and that the latter, while it strikes at a greater distance, and pervades conductors with much greater speed, can with difficulty be made to effect the slightest decompositions. Wollaston, it is true, decomposed water by means of it; but the experiment was performed of necessity on a scale too minute to permit of his ascertaining, whether there were any divellent polar attractions exercised towards the atoms, as in the case of the pile. The result was probably caused by mechanical concussion, or that process by which the particles of matter are dispersed when a battery is discharged through them. The opinion of Dr. Thomson, that the fluid of the pile is in quantity greater, in intensity less, than that evolved by the machine, is very inconsistent with the experiments of the chemist above mentioned, who, before he could effect the separation of the elements of water by mechanical electricity, was obliged to confine its emission to a point imperceptible to the naked eye. If already so highly intense, wherefore the necessity of a further concentration? Besides, were the distinction made by Dr. Thomson correct, the more concentrated fluid generated by a galvanic apparatus of a great many small pairs, ought most to resemble that of the ordinary electricity; but the opposite is the case. The ignition produced by a few large galvanic plates, where the intensity is of course low, is a result most analogous to the chemical effects of a common electrical battery. According to my view, caloric and electricity may be distinguished by the following characteristics. The former permeates all matter more or less, though with very different degrees of faci-It radiates through air, with immeasurable celerity, and distributing itself in the interior of bodies, communicates a reciprocally repellent power to atoms, but not to masses. Electricity does not radiate in or through any matter; and while it pervades

<sup>\*</sup> In whose Journal it was ordered to be printed, but, to prevent delay, it was published, by the author, in a separate paper, and forwarded by him to the editor of this Journal.

some bodies, as metals, with almost infinite velocity; by others, it is so far from being conducted, that it can only pass through them by a fracture or perforation. Distributing itself over surfaces only, it causes repulsion between masses, but not between the particles of the same mass. The disposition of the last-mentioned principle to get off by neighbouring conductors, and of the other to combine with the adjoining matter, or to escape by radiation, would prevent them from being collected at the positive pole, if not in combination with each other. Were it not for a modification of their properties, consequent to some such union, they could not, in piles of thousands of pairs, be carried forward through the open air and moisture; the one so well calculated to conduct away electricity, the other so favourable to the radiation of caloric.

Pure electricity does not expand the slips of gold-leaf, between which it causes repulsion, nor does caloric cause any repulsion in the ignited masses which it expands. But as the compound fluid extricated by galvanic action, which I shall call electro-caloric, distributes itself through the interior of bodies, and is evidently productive of corpuscular repulsion. It is in this respect more

allied to caloric than to electricity.

It is true, that when common electricity causes the deflagration of metals, as by the discharge of a Leyden jar, it must be supposed to insinuate itself within them, and cause a reaction between their particles. But in this case, agreeably to my hypothesis, the electric fluid combines with the latent caloric previously existing there, and, adding to its repulsive agency, causes it to overpower cohesion.\*

Sir Humphry Davy was so much at a loss to account for the continued ignition of wire at the poles of a voltaic apparatus, that he considers it an objection to the materiality of heat; since the wire could not be imagined to contain sufficient caloric to keep up the emission of this principle for an unlimited time. But if we conceive an accumulation of heat to accompany that of electricity throughout the series, and to be propagated from one end to the other, the explanation of the phenomenon in question is attended

by no difficulty.

The effect of the galvanic fluid on charcoal is very consistent with my views, since, next to metals, it is one of the best conductors of electricity, and the worst of heat, and would therefore arrest the last, and allow the other to pass on. Though peculiarly liable to intense ignition, when exposed between the poles of the voltaic apparatus, it seems to me it does not display this characteristic with common electricity. According to sir Humphry Davy, when in connexion with the positive pole, and communicating by a platina wire with the negative pole, the latter is

<sup>\*</sup> Possibly the electric fluid causes decompositions when emitted from an impalpable point (as in the experiments of Wollaston) because its repulsive agency is concentred between integral atoms, in a mode analogous to that here referred to; a filament of water in the one case, and of wire in the other, being the medium of discharge.

less heated than when, with respect to the poles, the situation of the wire and charcoal is reversed. The rationale is obvious: charcoal, being a bad conductor, and a good radiator, prevents the greater part of the heat from reaching the platina, when placed

between it and the source whence the heat flows.

I had observed that as the number of pairs in Volta's pile had been extended, and their size and the energy of the interposed agents lessened, the ratio of the electrical effects to those of heat had increased; till in De Luc's column they had become completely predominant; and, on the other hand, when the pairs were made larger and fewer (as in Children's apparatus) the calorific influence had gained the ascendancy. I was led to go farther in this way, and to examine whether one pair of plates of enormous size, or what might be equivalent thereto, would not exhibit heat more purely, and demonstrate it, equally with the eletric fluid, a primary product of Galvanic combinations. The elementary battery of Wollaston, though productive of an evanescent ignition, was too minute to allow him to make the observations which I had in view.

Twenty copper and twenty zinc plates, about nineteen inches square, were supported vertically in a frame, the different metals alternating at one half inch distance from each other. All the plates of the same kind of metal were soldered to a common slip, so that each set of homogeneous plates formed one continuous metallic superficies. When the copper and zinc surfaces, thus formed, are united by an intervening wire, and the whole immerged in an acid, or aceto-saline solution, in a vessel devoid of partitions, the wire becomes intensely ignited; and when hydrogen is liberated it usually takes fire, producing a very beautiful undulat-

ing, or corruscating flame.

I am contident, that if Volta and the other investigators of galvanism, instead of multiplying the pairs of galvanic plates, had sought to increase the effect by enlarging one pair as I have done, (for I consider the copper and zinc surfaces as reduced to two by the connexion) the apparatus would have been considered as presenting a new mode of evolving heat, as a primary effect independently of electrical influence. There is no other indication of electricity when wires from the two surfaces touch the tongue, than a slight taste, such as is excited by small pieces of zinc and silver laid on it and under it, and brought into contact with each other.

It was with a view of examining the effects of the proximity and alternation in the heterogeneous plates that I had them cut into separate squares. By having them thus divided, I have been enabled to ascertain that when all of one kind of metal are ranged on one side of the frame, and all of the other kind on the other side of it, the effect is no greater than might be expected from one pair of plates.

Volta, considering the changes consequent to his contrivance as the effect of a movement in the electric fluid, called the process

electro-motion, and the plates producing it electro-motors. But' the phenomena show that the plates, as I have arranged them, are calori-motors, or heat-movers, and the effect calori-motion. That this is a new view of the subject, may be inferred from the following passage in Davy's Elements. That great chemist observes, "When very small conducting surfaces are used for conveying very large quantities of electricity, they become ignited; and of the different conductors that have been compared, charcoal is most easily heated by electrical discharges\*, next iron, platina, gold, then copper, and lastly, zinc. The phenomena of electrical ignition, whether taking place in gaseous, fluid, or solid bodies, always seem to be the result of a violent exertion of the electrical attractive and repellent powers, which may be connected with motions of the particles of the substances affected. That no subtile fluid, such as the matter of heat has been imagined to be, can be discharged from these substances, in consequence of the effect of the electricity, seems probable, from the circumstance, that a wire of platina may be preserved in a state of intense ignition in vacuo, by means of the voltaic apparatus, for an unlimited time; and such a wire cannot be supposed to contain an inexhaustible quantity of subtile matter."

But I demand where are the repellent and attractive powers to which the ignition produced by the Calorimotor can be attributed? Besides, I would beg leave respectfully to inquire of this illustrious author, whence the necessity of considering the heat evolved under the circumstances alluded to as the effect of the electrical fluid; or why we may not as well suppose the latter to be excited by the heat? It is evident, as he observes, that a wire cannot be supposed to contain an inexhaustible supply of matter however subtile; but wherefore may not one kind of subtile matter be supplied to it from the apparatus as well as another; especially, when to suppose such a supply is quite as inconsistent with the characteristics of pure electricity, as with those of pure caloric?

It is evident from Mr. Children's paper in the Annals of Philosophy, on the subject of his large apparatus, that the ignition

produced by it was ascribed to electrical excitement.

For the purpose of ascertaining the necessity of the alternation and proximity of the copper and zinc plates, it has been men-The experitioned that distinct square sheets were employed. ments have since been repeated and found to succeed by Dr. Patterson and Mr. Lukens, by means of two continuous sheets, one of zinc, the other of copper, wound into two concentric coils or This, though the circumstance was not known to them, was the form I had myself proposed to adopt, and had suggested as convenient for a galvanic apparatus to several friends at the beginning of the winter; though the consideration above stated

† Especially to Dr. T. P. Jones, and Mr. Rubens Peale, who remember the suggestion.

<sup>\*</sup> The conclusions are drawn from experiments made by the electricity of the voltaic apparatus.

induced me to prefer for a first experiment a more manageable

arrangement

Since writing the above, I find that when, in the apparatus of twenty copper and twenty zinc plates, ten copper plates on one side are connected with ten zinc on the other, and a communication made between the remaining twenty by a piece of iron wire, about the eighth of an inch in diameter, the wire enters into a vivid state of combustion on the immersion of the plates. Platina wire equal to No. 18 (the largest I had at hand) is rapidly fused if substituted for the iron.

This arrangement is equivalent to a battery of two large galvanic pairs; excepting that there is no insulation, all the plates being plunged in one vessel. I have usually separated the pairs

by a board, extending across the frame merely.

in the downward passage of caloric through them.

Indeed, when the forty plates were successively associated in pairs, of copper and zinc, though suspended in a fluid held in a common recipient without partitions; there was considerable intensity of galvanic action. This shows that, independently of any power of conducting electricity, there is some movement in the solvent fluid which tends to carry forward the galvanic principle from the copper to the zinc end of the series. I infer that electrocaloric is communicated in this case by circulation, and that in non-elastic fluids the same difficulty exists as to its retrocession from the positive to the negative end of the series, as is found

It ought to be mentioned, that the connecting wire should be placed between the heterogeneous surfaces before their immersion, as the most intense ignition takes place immediately afterward. If the connection be made after the plates are immersed, the effect is much less powerful, and sometimes after two or three immersions the apparatus loses its power, though the action of the solvent should become in the interim much more violent. Without any change in the latter, after the plates have been for some time suspended in the air, they regain their efficacy. I had observed in a galvanic pile of three hundred pairs of two inches square, a like consequence resulting from a simultaneous immersion of the whole.\* The bars holding the plates were balanced by weights, as window-sashes are, so that all the plates could be very quickly dipped. A platina wire, No. 18, was fused into a globule, while the evolution of potassium was demonstrated by a rose-coloured flame arising from some potash which had been placed between the poles. The heat however diminished in a few seconds, though the greater extrication of hydrogen from the plates indicated a more intense chemical action.

Agreeably to an observation of Dr. Patterson, electrical excitement may be detected in the apparatus by the condensing electroscope; but this is no more than what Volta observed to be the consequence of the contact of heterogeneous metals.

<sup>\*</sup> See Plate. Fig. 3.

The thinnest piece of charcoal intercepts the caloric agent, whatever it may be. In order to ascertain this, the inside of a hollow brass cylinder, having the internal diameter two inches, and the outside of another smaller cylinder of the same substance, were made conical and correspondent, so that the greater would contain the less, and leave an interstice of about one-sixteenth of an inch between them. This interstice was filled with wood, by plugging the larger cylinder with this material, and excavating the plug till it would permit the smaller brass cylinder to be driv-The excavation and the fitting of the cylinders was performed accurately by means of a turning lathe. The wood in the interstice was then charred by exposing the whole covered by sand in a crucible to a red heat. The charcoal, notwithstanding the shrinkage consequent to the fire, was brought into complete contact with the inclosing metallic surfaces by pressing the interior cylinder further into the exterior one.

Thus prepared, the interior cylinder being made to touch one of the galvanic surfaces, a wire brought from the other galvanic surface into contact with the outside cylinder, was not affected in the least, though the slightest touch of the interior one caused ignition. The contact of the charcoal, with the containing metals probably took place throughout a superficies of four square inches, and the wire was not much more than the hundredth part of an inch thick, so that unless it were to conduct electricity about forty thousand times better than the charcoal, it ought to have been heated; if the calorific influence of this apparatus result from

electrical excitement.

I am led finally to suppose, that the contact of dissimilar metals, when subjected to the action of solvents, causes a movement in caloric as well as in the electric fluid, and that the phenomena of galvanism, the unlimited evolution of heat by friction, the extrication of gaseous matter without the production of cold, might all be explained by supposing a combination between the fluids of heat and electricity. We find scarcely any two kinds of ponderable matter which do not exercise more or less affinity towards each other. Moreover, imponderable particles are supposed highly attractive of ponderable ones. Why then should we not infer the existence of similar affinities between imponderable particles reciprocally? That a peculiar combination between heat and light exists in the solar beams, is evident from their not imparting warmth to a lens through which they may pass, as do those of our culinary fires.

Under this view of the case, the action of the poles in galvanic decomposition is one of complex affinity. The particles of compounds are attracted to the different wires agreeably to their susceptibilities to the positive and negative attraction, and the caloric leaving the electric fluid with which it had been combined, unites with them at the moment that their electric state is neu-

tralized.

As an exciting fluid, I have usually employed a solution of one part sulphuric acid, and two parts muriate of soda with seventy of water; but, to my surprise, I have produced nearly a white heat by an alkaline solution barely sensible to the taste.

For the display of the heat effects, the addition of manganese,

red lead, or the nitrates, is advantageous.

The rationale is obvious. The oxygen of these substances prevents the liberation of the gaseous hydrogen, which would carry off the caloric. Adding to diluted muriatic acid, while acting on zinc, enough red lead to prevent effervescence, the temperature

rose from 70 to 110 Fahrenheit.

The power of the calorimotor is much increased by having the communication between the different sheets formed by very large strips or masses of metal. Observing this, I rendered the sheets of copper shorter by half an inch, for a distance of four inches of their edges, where the communication was to be made between the zinc sheets; and, vice versa, the zinc was made in the same way shorter than the copper sheets where these were to communicate with each other. The edges of the shortened sheets being defended by strips of wood, tin was cast on the intermediate protruding edges of the longer ones, so as to embrace a portion of each equal to about one quarter of an inch by four inches. On one side, the tin was made to run completely across, connecting at the same time ten copper and ten zinc sheets. On the other side there was an interstice of above a quarter of an inch left between the stratum of tin embracing the copper, and that embracing the zinc plates. On each of the approaching terminations of the connecting tin strata was soldered a kind of forceps, formed of a bent. piece of sheet brass, furnished with a screw for pressing the jaws together. The distance between the different forceps was about The advantage of a very close contact was made two inches. very evident by the action of the screws; the relaxation or increase of pressure on the connecting wire by turning them being productive of a correspondent change in the intensity of ignition.

It now remains to state, that by means of iron ignited in this apparatus, a fixed alkali may be decomposed extemporaneously.\* If a connecting iron wire, while in combustion, be touched by the hydrate of potash, the evolution of potassium is demonstrated by a rose-coloured flame. The alkali may be applied to the wire in small pieces in a flat hook of sheet iron. But the best mode of application is by means of a tray made by doubling a slip of sheet iron at the ends, and leaving a receptacle in the centre, in which the potash may be placed covered with filings. This tray being

<sup>\*</sup> This evidently differs from the common mode of decomposing the fixed alkalies by galvanism: there the effect depends on electrical attractions and repulsions—here on the chemical agency of ignited iron produced extemporaneously in the galvanic circuit: this mode of operating appears to be new.

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substituted for the connecting wire, as soon as the immersion of the apparatus causes the metal to burn, the rose-coloured flame appears, and if the residuum left in the sheet iron be afterward thrown into water, an effervescence sometimes ensues.

I have ascertained that an iron heated to combustion, by a blacksmith's forge fire, will cause the decomposition of the hydrate

of potash.

The dimensions of the calorimotor may be much reduced without proportionably diminishing the effect. I have one of sixty plates within a cubic foot, which burns off No. 16, iron wire. A good workman could get 120 plates of a foot square within a hollow-cube of a size no larger. But the inflammation of the hydrogen which gives so much splendor to the experiment, can only be exhibited advantageously on a large scale.

### EXPLANATION OF THE PLATE.

A a. Fig. 1st. two cubical vessels, 20 inches square, inside. b b b b a frame of wood containing 20 sheets of copper, and 20 sheets of zinc, alternating with each other, and about half an inch apart. T T t t masses of tin cast over the protruding edges of the sheets which are to communicate with each other. Fig. 2, represents the mode in which the junction between the various sheets and tin masses is effected. Between the letters z, the zinc only is in contact with the tin masses. Between c c the copper alone touches. It may be observed, that, at the back of the frame, ten sheets of copper between cc, and ten sheets of zinc between zz, are made to communicate, by a common mass of tin extending the whole length of the frame, between T T: but in front, as in fig. 1, there is an interstice between the mass of tin connecting the ten copper sheets, and that connecting the ten zinc sheets. The screw forceps, appertaining to each of the tin masses, may be seen on either side of the interstice: and likewise a wire for The application of the rope, pulley, ignition held between them. and weights, is obvious. The swivel at S permits the frame to be swung round and lowered into water in the vessel a, to wash off the acid, which, after immersion in the other vessel, might continue to act on the sheets, encrusting them with oxide. Between p p there is a wooden partition which is not necessary, though it may be beneficial.

Fig. 3, represents an apparatus alluded to, page 419. It consists of a couronne des tasses, reduced to a form no less compact than that of the trough. Hollow parallelopipeds of glass are substituted for tumblers or cells. The plates are suspended to bars

counterpoised like window-sashes.

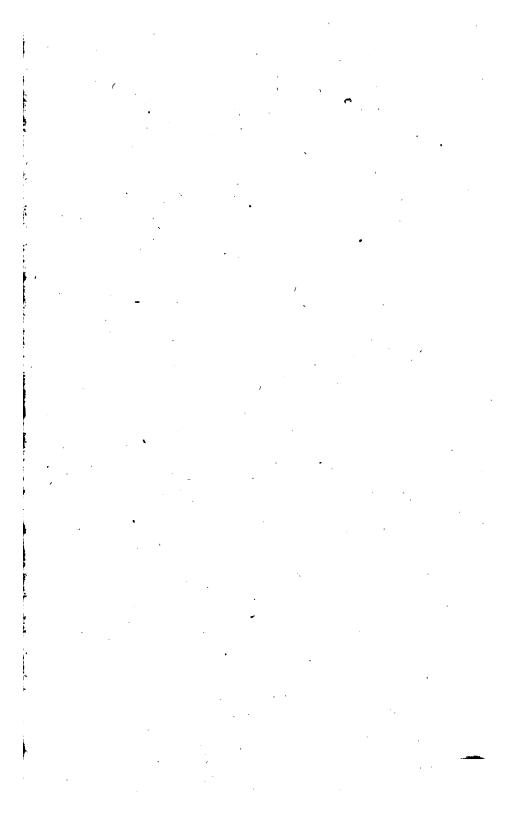
The advantages are as follows. The material is one of the best non-conductors, is easily cleansed, and is the most impervious to solvents. The fracture of one of the cups is easily remedied by a supernumerary. They may be procured (as in the United States)

where porcelain cannot be had. The shock from 300 pairs is such as few will take a second time. Some of the effects have already been stated.\*

At Fig. 4, one of the hollow glass parallelopipeds on an enlarg-

ed scale is represented.

<sup>\*</sup> The glasses may be had by applying to Edw. A. Pearson, No. 71 Cornhill, Boston.





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